U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-270 911

Limestone and Lime Neutralization of Ferrous Iron Acid Mine Drainage

Environmental Protection Agency, Rivesville, W Va

May 77

PB 270 011

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22151

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-77-101	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE: LIMESTONE AND LIME NEUTRALISATION OF FERROUS IRON ACID MINE DRAINAGE	5. REPORT DATE: May 1977 Issuing date
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): Roger C. Wilmoth	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Resource Extraction and Handling Division, Crown Mine Drainage Control Field Site, Box 999, Riversville, W. Va. 26588	10. PROGRAM ELEMENT NO. 1BB610
	11. CONTRACT/GRANT NO. 05-03-01A-07-01D
12. SPONSORING AGENCY NAME AND ADDRESS: Industrial Environmental Research Laboratory-Cin., OH, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED: Final 1/75 - 1/76
	14. SPONSORING AGENCY CODE: EPA/600/12
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

The U.S. Environmental Protection Agency conducted a 2-yr study on hydrated lime and rock-dust limestone neutralisation of acid mine drainage containing ferrous iron at the EPA Crown Mine Drainage Control Field Site near Riversville, West Virginia.

The study investigated optimisation of the limestone process and its feasibility in comparison with hydrated lime treatment. Operating parameters, design factors, and reagent costs for both processes were determined. Effluent quality was considered of prime importance in these investigations. Coagulants were considered essential to successful thickener operation for both lime and limestone treatment. Effluent iron, suspended solids, and turbidity values could be maintained below 3 mg/l, 10 mg/l, and 10 JTU, respectively, using coagulant addition.

Although the limestone process was demonstrated to be technically effective in ferrous iron treatment situations, the process was judged to be less efficient overall in comparison with lime neutralisation. The reaction and aeration detention time requirements for the limestone process were two to three times that for the lime process and overshadowed the reagent usage cost advantage of the limestone process. The limestone process was thus judged unfeasible for general application in ferrous iron acid mine drainage situations.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Limestone Calcium hydroxides Neutralising Drainage-mine (excavations) Cost comparison Surface drainage	Acid mine drainage Coal mine drainage Ferric iron West Virginia	13B

18. DISTRIBUTION STATEMENT: Release to public	19. SECURITY CLASS (This Report): Unclassified	21. NO. OF PAGES: 118
	20. SECURITY CLASS (This page): Unclassified	22. PRICE: NTIS

EPA Form 2220-1 (9-73)

* U.S. GOVERNMENT PRINTING OFFICE: 1977-757-056/6435 Region No. 5-11

EPA-600/2-77-101
May 1977

LIMESTONE AND LIME NEUTRALIZATION OF FERROUS IRON ACID MINE DRAINAGE

by

Roger C. Wilmoth
Resource Extraction and Handling Division
Crown Mine Drainage Control Field Site
Rivesville, West Virginia 26588

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

IA

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report evaluates the use of two commonly available neutralizing agents--limestone and lime--for use in the treatment of acid mine drainage (AMD), which is an industrial waste most closely associated with the mining of coal. This study deals specifically with AMD where the iron is in the ferrous state, which is the most difficult situation to treat. Because of the recent emphasis on immediate expansion of the coal industry, the technology for the abatement of pollution from the mining operations needs reliable definition. The documentation of the cost, effectiveness, and feasibility of the use of lime and of limestone is included in this report. As such, this data will be of interest to regulatory agencies, individuals involved in AMD treatment research, and--perhaps most importantly--to industry as an aid to the design and/or modification of treatment facilities. For further information contact the Resource Extraction and Handling Division.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

The U.S. Environmental Protection Agency (EPA) conducted a 2-yr study on hydrated lime and rock-dust limestone neutralization of acid mine drainage containing ferrous iron at the EPA Crown Mine Drainage Control Field Site near Rivesville, West Virginia.

The study investigated optimization of the limestone process and its feasibility in comparison with hydrated lime treatment. Operating parameters, design factors, and reagent costs for both processes were determined. Effluent quality was considered of prime importance in these investigations. Coagulants were considered essential to successful thickener operation for both lime and limestone treatment. Effluent total iron, suspended solids, and turbidity values could be maintained below 3 mg/l, 10 mg/l and 10 JTU, respectively, by using coagulant addition.

Although the limestone process was demonstrated to be technically effective in ferrous iron treatment situations, the process was judged to be less efficient overall in comparison with lime neutralization. The reaction and aeration detention time requirements for the limestone process were two to three times that for the lime process and overshadowed the reagent usage cost advantage of the limestone process. The limestone process was thus judged unfeasible for general application in ferrous iron acid mine drainage situations.

This report covers a period from January 1974 to January 1976.

CONTENTS

Foreword iii
Abstract iv
List of Figures vi
List of Tables viii
Acknowledgments x
1. Introduction 1
2. Conclusions 2
3. Recommendations 5
4. Procedures 6
5. Results 10
References 90
Glossary 94

FIGURES

Number		Page
1	Schematic flow diagram for the EPA neutralization facility	17
2	Titration curves for lime and limestone	19
3	Theoretical ion solubility as a function of pH	21
4	Effect of pH on ferrous iron solubility	23
5	Observed solubilities as a function of initial pH	24
6	Observed solubility of ions during continuous-flow studies	25
7	Comparison of settling trends at pH 6.5 and pH 9.5	27
8	Settling trends for lime neutralization	30
9	Settling trends for limestone neutralization	31
10	Settling trends for combination limestone-lime neutralization	32
11	Comparison of settling trends at pH 7	33
12	Sludge percent solids @ 1 hr as a function of pH	35
13	Supernatant turbidity @ 1 hr as a function of pH	36
14	Sludge percent solids @ 24 hr as a function of pH	37
15	Supernatant turbidity @ 24 hr as a function of pH	38
16	Batch-scale combination limestone-lime feasibility test	40
17	Effect of the treatment pH on lime-usage costs	68
18	Sludge volume and effluent turbidity as functions of pH	69
19	Underflow solids concentration and dry solids production for lime neutralization	70
20	Trend of the sludge solids during continuous sludge recycling with no sludge discharge	86

FIGURES (CONT'D)

Number		Page
51	Ferrous decline at various pH's for the EPA Crown discharge	88
52	Average oxidation rates as a function of pH	91

TABLES

Number		Page
1	Typical Detention Times	14
2	Crown Water Quality Data, 7/74 Thru 6/75	15
3	Manufacturers Chemical Analyses of Lime and Limestone	16
4	Spectrochemical Analysis of Cermany Valley Limestone	17
5	Sieve Analyses of As-Received Lime and Limestone	17
6	Theoretical Ksp Constants for AMD Hydroxide Compounds	20
7	Results Comparison as Related to Treatment pH	28
8	Results Comparison as Related to Settling Time	29
9	Combination Limestone-Lime Laboratory Study	39
10	Research Plan for Limestone Investigations	42
11	Neutralization Data Summaries for Limestone @ pH 6.5 and 1 Liter/Sec	43
12	Chemical Analyses From the Limestone Neutralization Studies	44
13	Limestone Neutralization Investigating Increased Detention Times	48
14	Limestone Neutralization With Sulfuric Acid Injection	49
15	Limestone Neutralization Comparing 0.5 Liter/Sec vs 1 Liter/Sec	50
16	Limestone Neutralization With Hydrogen Peroxide Addition	52
17	Limestone Neutralization With Sludge Recycle	53
18	Limestone Neutralization With Increased Recycle Rates	55
19	Limestone Neutralization With Two Aerators in Series	57

TABLES (CONT'D)

Number		Page
20	Limestone Neutralisation to pH 7 Using Two Aerators	59
21	Limestone Neutralisation Using Two Aerators and Coagulants @ 0.9 Liter/Sec	60
22	Limestone Neutralisation Using Two Aerators and Coagulants @ 0.9 Liter/Sec	61
23	Research Plan For Lime Neutralisation	64
24	Characteristic Operational Data for Lime Neutralisation Studies	65
25	Characteristic Chemical Analyses for Lime Neutralisation Studies	66
26	Lime Neutralisation Using Sludge Recycle	71
27	Chemical Analyses From the Lime Neutralisation Studies	72
28	Lime Neutralisation Investigating Recycling Rates	76
29	Lime Neutralisation Using Coagulant Addition	77
30	Lime Neutralisation Using Coagulant Addition @ pH 8 vs pH 7	79
31	Lime Neutralisation With Coagulants Comparing Sludge Recycle vs No Recycle	80
32	Lime Neutralisation @ pH 9 Using No Aeration (Ferrous Precipitation)	82
33	Lime Neutralisation Using No Aeration With Coagulant Addition	83
34	Lime Neutralisation; Aeration vs No Aeration	84

ACKNOWLEDGMENTS

Thanks are extended to Ronald D. Hill, Eugene F. Harris, Robert B. Scott, James L. Kennedy, Loretta J. Davis, Walter E. Grube, Jr., Paul M. Moore, Robert M. Michael, Ralph B. Herron, Paula G. Arnett, Cathy J. Scott, Joan R. Allender, and Frank J. Deafore for their helpful suggestions and willing assistance during the course of these investigations.

A special thanks is extended to J. Randolph Lipscomb and Harry L. Armentrout for their insight and invaluable contributions to the success of this project.

The cooperation of Ray Henderson, Vince Ream, Ed Moore, Mike Ryan, and Hershel Travis of Consolidation Coal Company is greatly appreciated.

SECTION 1
INTRODUCTION

The Environmental Protection Agency's (EPA) Crown Mine Drainage Control Field Site facility, located near Morgantown, West Virginia, was established in 1972 to investigate the treatment requirements of predominately ferrous iron acid mine drainage. This was a partial follow-up of earlier studies[1] by the same staff at Norton, West Virginia, where the iron in the acid mine drainage (AMD) was in the ferric state.

EPA employees designed the Crown facility and performed most of the construction work. Contracts were awarded for the plant building shell, drying beds, lagoon, storage bins, and miscellaneous earthwork, and EPA personnel completed the construction including wiring, plumbing, instrumentation, and fabrication.

At present, lime neutralization is the commonly accepted method for treatment of AMD discharges. Lime treatment has several disadvantages:

- It produces a low-density, high-volume sludge.
- Its highly reactive nature provides high potential for accidental overtreatment.
- As a refined product, it is moderately expensive and is in increasingly short supply.

Earlier studies by EPA and others have indicated that limestone treatment (also combination limestone/lime) has advantages over lime in certain situations. Most important of these advantages are:

- Production of a low-volume, high-density sludge.
- Cheaper raw-materials costs.
- Cheaper usage costs in some instances.

These processes needed to be investigated under ferrous iron conditions before they could be fully evaluated. This report documents the results of research conducted to evaluate the lime and limestone processes (plus bench-scale studies on combination limestone/lime) under ferrous iron conditions.

SECTION 8
CONCLUSIONS

LIMESTONE TREATMENT OF FERROUS IRON AMD

Limestone utilization efficiencies were below 30 percent for ferrous iron acid mine drainage neutralization to pH 6.5, which was about the highest pH obtainable without sludge recycling. Effluent quality from the thickener was terrible under the pH 6.5 conditions.

Recycling sludge at a rate of 20 percent of the influent flow rate increased the utilization efficiency of limestone to the 50-percent range. Effluent quality was still poor.

The use of two aerators in series provided adequate detention time for ferrous iron oxidation. At least 4-hr detention time was necessary to reduce the ferrous iron level from 270 to 2.4 mg/l at pH's near 7. The combination of increased aeration time, better mixing, and sludge recycling enabled limestone treatment to ph's as high as 7.4. Effluent suspended solids (40 mg/l) and turbidity (60 JTU) were still high. Neutralization efficiencies ranged from 50 to 80 percent.

Addition of coagulants reduced effluent iron levels (from 20 to 1 mg/l), lowered turbidities (from 60 to 12 JTU), and improved suspended solids (from 40 to 9 mg/l). The coagulants greatly diminished pH probe fouling problems, which were generally severe below pH 7.5.

The most satisfactory process operation involved incorporating a 20-percent sludge recycle rate, maintaining pH's near 7.4, furnishing 30-min detention time with vigorous mixing in the reactor, providing between 4 and 6 hr of detention time in the aeration system, and injecting coagulants at about a 7-mg/l rate. Reagent costs for this process were approximately 1.3 cents/cu m (5 cents/1000 gal) for limestone plus approximately 2.6 cents/cu m (10 cents/ 1000 gal) for coagulant. Coagulant addition was not optimized. The thickener was most effective in clarification around 0.05 liter/sec/sq m (0.07 gpm/sq ft) of surface area.

LIME TREATMENT OF FERROUS IRON AMD

Optimum overall operation of the EPA treatment system was at pH 8. At this pH, probe fouling problems were almost nonexistent, effluent clarity was improved, and iron oxidation was complete. Reagent cost was increased over 25 percent by treating to pH 8 rather than pH 7; an additional 40-percent cost increase was incurred by treating to pH 8.5 rather than to pH 8.

The thickener appeared to function most satisfactorily when the influent suspended solids were between 5,000 and 10,000 mg/l. Sludge recycling was employed to increase the influent solids to this range. Thickener effluents contained between 4 and 10 mg/l of suspended colloidal iron.

Coagulants were very effective in improving the thickener effluent quality. Iron values were consistently below 2 mg/l using coagulants at pH 8.

Precipitating the iron without oxidation offered few advantages over the oxidized version of the neutralization process. For ferrous precipitation, pH's had to be elevated to around pH 9, resulting in an increase in lime cost of 30 percent as compared to ferric treatment to pH 8. The ferrous hydroxide sludge occupied more than 1.5 times the volume of the ferric sludge. Thickener effluent quality was significantly better in the ferric situation.

Lime treatment to pH 8 required approximately 7-min reaction time and less than 2-hr oxidation time (utilizing a sludge recycling rate below 20 percent of the influent rate) and required coagulant addition at a rate under 5 mg/l. Reagent costs for this process were approximately 2.9 cents/cu m (11 cents/1000 gal) for lime plus 1.9 cents/cu m (7 cents/1000 gal) for coagulant. Coagulant addition was not optimized. Sludge settling rates with coagulants were greater than 4 cm/sec (8 ft/hr) for unhindered settling.

COMPARISON OF LIMESTONE VS LIME

Limestone treatment of ferrous iron acid mine drainage involves reagent usage costs somewhat less than is required for lime treatment. Overall costs of the limestone process must include the very large reaction and oxidation vessel size and increased power requirements. These and other operational considerations render the limestone process to be considered unfeasible for general application to AMD waters containing over 50 mg/l of ferrous iron.

IRON OXIDATION

An average oxidation rate design factor of 2 mg/l per min is suggested for lime neutralization aeration facilities with influent ferrous levels below 300

mg/l. On-site tests should be made to better determine the actual rate for the specific conditions before proceeding to final design. It is imperative that sufficient mixing capability be incorporated to provide enough top-to-bottom turbulence to prevent solids accumulation in the aeration tank.

SECTION 5
RECOMMENDATIONS

Accurate and reliable design criteria for oxidation time requirements for acid mine waters are not available. The same applies to thickener design criteria. A study should be undertaken of existing AMD neutralization facilities to determine if an accurate model of these processes could be developed.

Sludge disposal from AMD treatment processes has received little research effort to date. Since as much as 10 percent of the influent AMD can exit from the plant as sludge, a significant effort to evaluate the disposal alternatives, costs, and environmental effects is essential.

If the AMD should contain toxic pollutants, it is logical to assume that at least some of these would be removed by neutralization. In this case, the sludge would contain relatively high concentrations of toxic materials and disposal considerations become even more critical.

The fact that the environment suffers from AMD pollution is unquestionable; however, the alternative offered by lime and limestone treatment is the introduction of high calcium and sulfate concentrations into the receiving stream. An evaluation should be made of the overall long-term environmental and economic effects of increased calcium and sulfate levels and of suggested alternatives such as reverse osmosis, ion exchange, lime-soda softening, and alumina-lime-soda treatment.

SECTION 4
PROCEDURES

DEFINITIONS

Definitions and an explanation of the calculations used in this report are presented in the Glossary.

DESCRIPTION OF FACILITY

Acid mine water was obtained from the Stewarts Run borehole pump of Christopher Coal Company that pumped water from the Pittsburgh Coal Seam located approximately 85 m (280 ft) below the surface. This pump removed water from an abandoned section of Mine 91 to prevent the drainage from entering an active section of the mine. The borehole pump discharged approximately 32 liters/sec (500 gpm) into a 3.8-cu m (1000-gal) concrete reservoir constructed from a burial vault. The water used by the NPA facility was pumped from the reservoir to the treatment plant--a distance of about 366 m (1200 ft)--through a 102-mm (4-in) plastic pipe at a pressure of 480 kN/sq m (70 psi).

The AMD flowed through the neutralization facility as illustrated in Figure 1. Processes A and B were identical in every respect. By having a dual system such as this, it was possible to use one side as a control and the other side as the variable and thus expedite the research efforts. The dual system allowed immediate evaluation of the isolated variable under study. All AMD transfer lines were 25-mm (1-in), Schedule 40 PVC. The sludge lines were 13-mm (½-in) plastic roll piping. PVC in-line strainers removed large particulate matter from the AMD prior to entering the pressure regulators. Fisst-O-Matic Model PRO75V pressure regulators were used to maintain relatively constant downstream pressures to reduce flow fluctuations. G-E Invalco Model W3/1000 turbine flow meters with Model W315 totalisers and rate indicators totalised gallonage treated and displayed instantaneous rate of flow. Accuracy of these meters was better than 1 percent of the full-scale flow of 10.3 liters/sec (64 gpm).

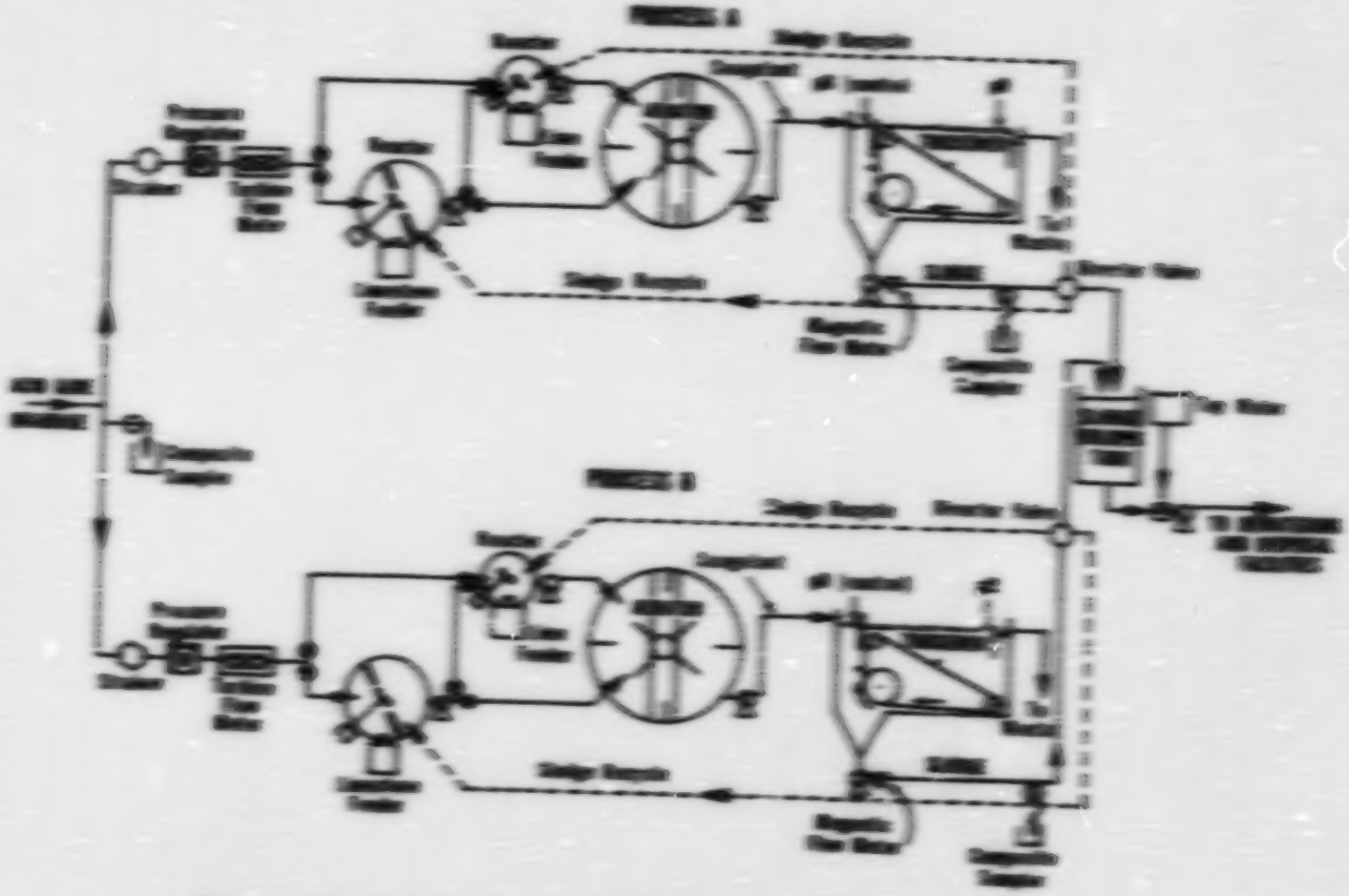


Figure 1. Schematic Flow Diagram for the CFR monofluidizer facility.

From the turbine meters, water could be channeled either:

1) Into the lime reactor, the aerator, and the thickener; or
2) Into the limestone reactor, the aerator, and the thickener; or
3) Into the limestone reactor, the lime reactor, the aerator and the thickener.

The lime reactor tanks were type 304 stainless steel with effective capacities of 454 liters (120 gal) and were equipped with Lightnin' Model NB-7, 3-hp, 1750-rpm mixers. High-density polyethylene tanks with 9.5-mm (3/8-in) thick walls and effective capacities of 3785 liters (1000 gal) were used for the limestone reactors. Lightnin' NB-7 mixers were installed on independent mounts for use with the polyethylene tanks. In later studies, the NB-7 mixers on the limestone reactors were replaced by 3-hp, 350-rpm, Lightnin' ND-4B mixers to obtain increased turbulence. The NB-7 system provided a mixing (pumping) rate of 93 liter/sec (1470 gpm); the ND-4B pumped 360 liter/sec (5710 gpm). The limestone reactors were equipped with two baffles per tank. Each baffle consisted of a metal outside support frame surrounding a 168-cm by 36-cm (66-in by 14-in), 14 x 14-mesh, 304-stainless steel screen. The screen baffles served to improve mixing efficiency and to abrade the limestone particles in order to remove reaction coatings.

BIF Model 25-06 helix-type volumetric dry feeders with variable-speed drives were used to feed both hydrated lime and rock-dust limestone into the respective reactors. The hoppers on top of the dry feeders held 0.2 cu m (7.8 cu ft) of material. Syntron Model V-20 vibrators were bolted to the side of each hopper to prevent bridging. The vibrators operated whenever the dry feeders were operating. Typical observed dry feeder accuracies were about ± 5 percent on a weight basis. The operating time for each dry feeder was accumulated on Engle Model HK300A6 time totalisers reading directly in minutes. These units were equipped with dynamic braking circuitry to prevent the timers from coasting after the dry feeders stopped.

The lime and limestone dry feeders were refilled automatically from 36-tonne (40-ton) capacity Butler bolted-steel silos equipped with Vibra-screw bin activators to prevent bridging. Jeffrey screw conveyors with 19-cm (6-in) screws transported the neutraliser from the silos to the top of the dry feeders. Monitor-brand bin level indicators were mounted in the dry feeder hoppers to activate the conveyors when the level dropped.

The storage silos were periodically pneumatically filled from 18-tonne (20-ton) supply trucks. Butler Model CBG-90 bin-vent filters were mounted on top of the silos to prevent dust from escaping while the tanks were being loaded.

The neutralized water was pumped from the reactors into the aerators. The aeration tanks were 3 m (10 ft) in diameter by 1.8 m (6 ft) high with a nominal water depth of 100 cm (3.25 ft); they contained 6800 liters (1800 gal). Four 25-cm (10-in) solid baffles were installed at equal spacing around the periphery of the tank. The tank itself was constructed of 6.4-mm (¼-in) hot-rolled steel coated with epoxy. Lightnin' Model LAR-10, 1 hp, fixed-mount, surface aerators were installed on top of the aeration tanks. These aerators were designed to transfer 1.8 kg/hr (4 lb/hr) of oxygen under standard conditions.

Although the aerators were quite satisfactory in oxygen transfer, they lacked sufficient top-to-bottom turbulence to keep heavier particles suspended. This problem was most prevalent during limestone treatment studies where a sizable accumulation of solids occurred in the bottom of the aeration tank and thus decreased the effective detention time. A bottom-mixing prop was installed on the aerator shaft later in the studies to successfully decrease the solids accumulation problem.

After aeration, the treated water was pumped into the thickener for clarification and sludge removal. FMC Link-Belt, Type-H thickeners were used. These thickeners were 5.7 m (18.75 ft) long, 2.4 m (8.0 ft) wide, and 2.7 m (9.0 ft) high (excluding sludge hoppers) and had an effective capacity of 34.8 cu m (9200 gal). Adjustable effluent weirs allowed the effective depth to be varied from 2.7 m (9 ft) to 1.8 m (6 ft). Rakes moving at 0.005 m/sec (1 fpm) pushed the sludge into a collection hopper on the influent end of the thickener. The sludge hopper extended approximately 1.6 m (5.25 ft) below the floor level of the thickener and held 3.4 cu m (900 gal) of sludge. At 1 liter/sec (15.85 gpm), the surface overflow rate was 0.07 liter/sec/sq m (0.11 gpm/sq ft).

Sludge was removed from the thickeners by timer-controlled centrifugal pumps. Continuous removal was not possible because the lines became plugged at low-flow rates. It was therefore necessary to pump the sludge for short durations at high-flow rates. A Tork Model 1EMB0C1 repeating-cycle timer

with a 15-min full-cycle time and 60 adjustable tabs to regulate on-off time controlled the pumping duration and frequency. Typically, in non-recycling situations, the sludge pumps operated 10 percent of the time (on 0.6 min and off 5.4 min). Sludge pumping rates were about 0.3 liter/sec (5.9 gpm) through a 13-mm (½-in) line corresponding to a linear flow velocity of 2.7 m/sec (9 fps).

Sludge recycling was accomplished by utilizing Eagle Signal Series HP700, adjustable-duration pulse-timers to control a pneumatically operated diverter valve in the sludge line. When the Tork timer activated the sludge pump, it simultaneously activated the Eagle pulse-timer. Sludge was recycled into the appropriate reactor until the Eagle timer timed-out and switched the sludge diverter valve in the waste direction.

Initially, Fischer 4404 diverter valves were used for recycling sludge. These valves had a 316-stainless steel body and ball with teflon seats. During limestone sludge recycle studies, the tiny unreacted limestone particles wedged between the teflon seats and the ball and scored both the seat and the ball in just a couple of weeks of operation. Later, these valves were replaced with Model 2600 NPT Red Valves with hypalon liners and PVC end caps.

Sludge flow was measured by Brooks Model 7185FB1IKA 13-mm (½-in) magnetic flow meters that totalized gallonage and displayed instantaneous rate-of-flow (Model 7300B1A2C signal converters and Model 2540B1A4A1A1 totalizers). Accuracy of these magnetic flow meters was 0.9 percent of the full-scale indication of 0.63 liter/sec (10 gpm).

Since each magmeter was placed before the diverter valve, the output was indicative of total sludge flow. To independently totalize the sludge quantity being recycled and the quantity going to waste, the magmeter signal converter output was channeled through a relay that switched (at the same time the diverter valve switched) from one totalizer to another.

The waste sludge from both thickeners was pumped into a 1.5-cu m (400-gal) reservoir located immediately adjacent to the thickeners. When the sludge level reached the top of the reservoir, an automatic sequencer-controlled pump transferred the sludge to disposal facilities and then flushed the sludge lines with approximately 150 liters (40 gal) of tap water. Sludge flow to the disposal facilities was initially measured by volumetrically determining the flow rate and multiplying by pumping time. Operating time of

the pump was recorded on an Eagle elapsed-time meter. Later, this flow was totalised electronically by remote slave counters on each magmeter waste totaliser. Typical pumping rates to the disposal facilities were 1.1 liter/sec (17 gpm) through a 25-mm (1-in) roll plastic line corresponding to a linear flow velocity of 2.1 m/sec (6.8 fps).

Both lime and limestone feed could be controlled either manually or automatically. Automatic control was accomplished by Universal Interloc (Unitec) Model 1001 pH recorder-controllers that utilised on-off type control. The pH controllers turned the dry feeders on when the pH dropped below the set point and off when the pH increased beyond the set point. In order to reduce probe fouling, the pH probes (Unitec Model 301 immersion-type) were placed in the influent area of the thickener. Probes that were placed in the reactors fouled within a few hours. Even in the thickener, the probes fouled severely at pH's below 7.5. It was necessary to clean the probes with HCl as often as three times per day at the lower-pH conditions. It took the probes approximately 1 hr to recover from each acid cleaning. Neutralising the probes in a pH 10 Na_2CO_3 solution hastened the probe recovery. At pH levels above 7.5, probe fouling was not a problem and cleaning was routinely done once a day.

Effluent pH was monitored by similar Unitec equipment with the pH probes placed immediately in front of the thickener effluent weir.

Both influent (control) and effluent pH's for processes A and B were recorded on Hewlett-Packard Model 7100B strip chart recorders. In the normal mode of operation, the control set-point on the influent pH meter was adjusted until the desired effluent pH was achieved. Generally, the entire system could be changed from one pH to another and stabilised within 36 hr. The pH control system worked extremely well, as the effluent pH could be maintained within $\pm$ 0.1 pH for extended periods of time. The design flow rate through each process was 1 liter/sec (15.9 gpm).

All process equipment was located indoors to isolate the variable of weather from the data evaluation.

PHYSICAL MEASUREMENTS

Flow and Reagent Usage

Water and sludge flow rates and quantities were measured by turbine meters and magnetic flow meters, respectively, as previously described. Reagent usage was calculated by collecting and weighing a 3-min sample from

the dry feeders at the beginning and end of each data set and averaging the values. The average rate per minute was multiplied by the number of minutes of dry feeder operation to determine the quantity of neutralising agent used. These reagent data were then related to the water quantity and influent and effluent acidity and alkalinity values to calculate the various parameters of interest such as usage, stoichiometric addition rate, and utilization efficiency. Definitions and details of these calculations are presented in the Glossary.

Water Sampling

The water quality from the borehole pump was quite variable. Fluctuations in influent acidity were as large as 50 percent in a 24-hr period. Initially, the beginning and ending acidities for each data set were averaged before being used in data calculations. Later, an automatic composite sampler was built and installed to provide more reliable influent water quality data.

Sludge Settling Rates

Sludge samples were placed in 1000-ml graduates and the sludge/supernatant interface was recorded as a function of time. In the case of limestone, as well as lime at low pH's, a definite interface never clearly developed during settling. In these cases, it was possible to observe the buildup of solids in the bottom of the graduate.

Sludge Sampling

Representative sludge samples were quite difficult to obtain from the process. Generally, the sludge was pumped in short-duration intervals on the timed-basis previously described. Considerable variation in sludge density was observed from the beginning to the end of the pumping cycle. All attempts were made to sample near the midpoint of the cycle. Later, automatic composite samplers were built and installed in the sludge lines at the discharges of the thickener hoppers.

The clarifier rakes moved the sludge consistently to the edge of the 3400-liter (900-gal) sludge hopper. Movement of the sludge from the top edge of the hopper down the steep sides to the pump intake was often erratic and thus created difficulties in obtaining representative samples. This was not an operational problem but merely presented difficulties in data evaluation.

Detention Times of the Various Vessels

Detention time determinations were made by instantaneously injecting either salt or acid into the inlet of the vessel and monitoring the effluent conductivity until it returned to a base level. The mean probable detention time was calculated from a plot on probability paper (see Glossary for explanation of calculation) and represents the point in time when the centroid of the tracer mass passed through the vessel. Results of these studies are in Table 1. The tracer appeared almost immediately in the effluents from all reactors and aerators because of the mixing capability of these vessels. In the thickeners, however, the first visible trace occurred at 120 min at both 18.9-liter/m (5-gpm) and 96.8-liter/m (15-gpm) flow rates with the sludge rakes operating. The sludge rakes significantly affected mixing in the thickeners. In a static thickener with the rakes off, it took 90 hr after tracer injection for the tracer to diffuse sufficiently to increase the conductivity at the discharge end of the thickener to 500 micromhos/cm; with the rakes on, the same conductivity was attained in 14 hr.

PROCEDURES FOR CHEMICAL ANALYSES

Conductivity and pH were measured potentiometrically. Total iron, aluminum, magnesium, manganese, and calcium were determined by atomic absorption spectrophotometry.[2] Sulfate was measured by adding barium to precipitate the sulfate and analyzing for residual dissolved barium in the supernatant by atomic absorption.[3] Precipitation of the barium was accelerated by centrifuging. EPA methods[4] were used for total solids, suspended solids, alkalinity, and turbidity determinations. Ferrous iron was determined by colorimetrically titrating potassium dichromate against a p-Diphenylamine sulfonic acid sodium salt indicator.[4] A YSI Model 51 dissolved oxygen ($D.O._2$) meter was used for D.O. measurements. The Salotto acidity method[5] was used, in which hydrogen peroxide is added to oxidize the metals; a room-temperature titration is then made to pH 7.3.

CHARACTERISTICS OF REACTANTS

Mine 33 Borehole Discharge

Table 2 presents the typical chemical quality of the AMD used for these studies.

| | | |

| | | |

Lime and Limestone

The limestone and hydrated lime used in this study were obtained from Germany Valley Limestone Company, Riverton, West Virginia. In order to obtain the smallest particle size commercially available, the rock-dust form of limestone was used. All tests in this study were made using the hydrated form of lime.

Table 3 presents the manufacturer's chemical analyses and cost for lime and limestone.

Table 3. MANUFACTURER'S CHEMICAL ANALYSIS OF LIME AND LIMESTONE

Parameter	Hydrated lime,[a] minimum % composition	Rock-dust limestone,[b] minimum % composition
CaO	72.00	53.0
MgO	0.70	0.38
$CaCO_3$ equivalent	130	90.6
SiO_2	-	0.49

[a]Lime cost $38.58/tonne ($35.00/ton) or 3.86 cents/kg (1.75 cents/lb) delivered in bulk.

[b]Limestone cost $12.13/tonne ($11.00/ton) or 1.21 cents/kg (0.55 cents/lb) delivered in bulk.

A spectrochemical analysis of the limestone was made by Bituminous Coal Research and is reported in Table 4. A dry sieve analysis of as-received lime and limestone is presented in Table 5.

Table 4. SPECTROCHEMICAL ANALYSIS OF GERMANY VALLEY LIMESTONE (percent)

Loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	Na_2O	K_2O	MnO_2
43.0	1.0	0.43	0.15	1.16	97.0	0.04	0.02	0.1	0.03

Table 5. SIEVE ANALYSES (DRY) OF AS-RECEIVED LIME AND LIMESTONE

Screen size	Hydrated lime, percent passing	Rock-dust limestone, percent passing
50 mesh (0.297 mm)	98.9	97.7
100 mesh (0.149 mm)	62.9	83.6
200 mesh (0.074 mm)	45.0	56.6
400 mesh (0.037 mm)	13.3	19.7
Percent not passing sieve	4.4	0.1

SECTION 5
RESULTS

While plant construction was underway, several bench-scale batch tests were performed to provide basic data and guidance for full-scale, continuous-flow tests to be performed later.

BENCH-SCALE BATCH TESTS

Titration Curves

A typical titration curve illustrating the comparative quantities of limestone and lime required to increase pH is given in Figure 2. The flat response in the limestone curve above pH 6 demonstrates two major problems in the use of limestone--i.e., the inability to produce the high pH's necessary for rapid iron oxidation and the difficulty of efficient control of the reaction to prevent high reagent usage. The titrations were repeated on samples in which hydrogen peroxide had been added to preoxidize the iron. Above pH 7.5, the lime curves converge, indicating that iron oxidation had occurred (in the ferrous sample) and the vast majority of potential acidity had been released and was available for reaction with the lime titrant. In the case of limestone, since the acidity present in the form of ferrous iron is not released until the iron oxidizes and hydrolyses, the ferric situation should require a greater quantity of limestone as more acidity is available for reaction with the titrant. This was not the case, however, as shown on the graph where the ferric pH's were higher (above 2.0 g) than the ferrous values for equal titrant additions. This same condition was duplicated in later continuous-flow studies. For reasons not understood, limestone reacts more completely in the ferric iron situation.

Solubilities of the Chemical Constituents of AMD

A review of current literature supplied solubility product (Ksp) values for solubility calculations. Table 6 lists these values and Figure 3 shows the concentration of the ions as a function of pH.

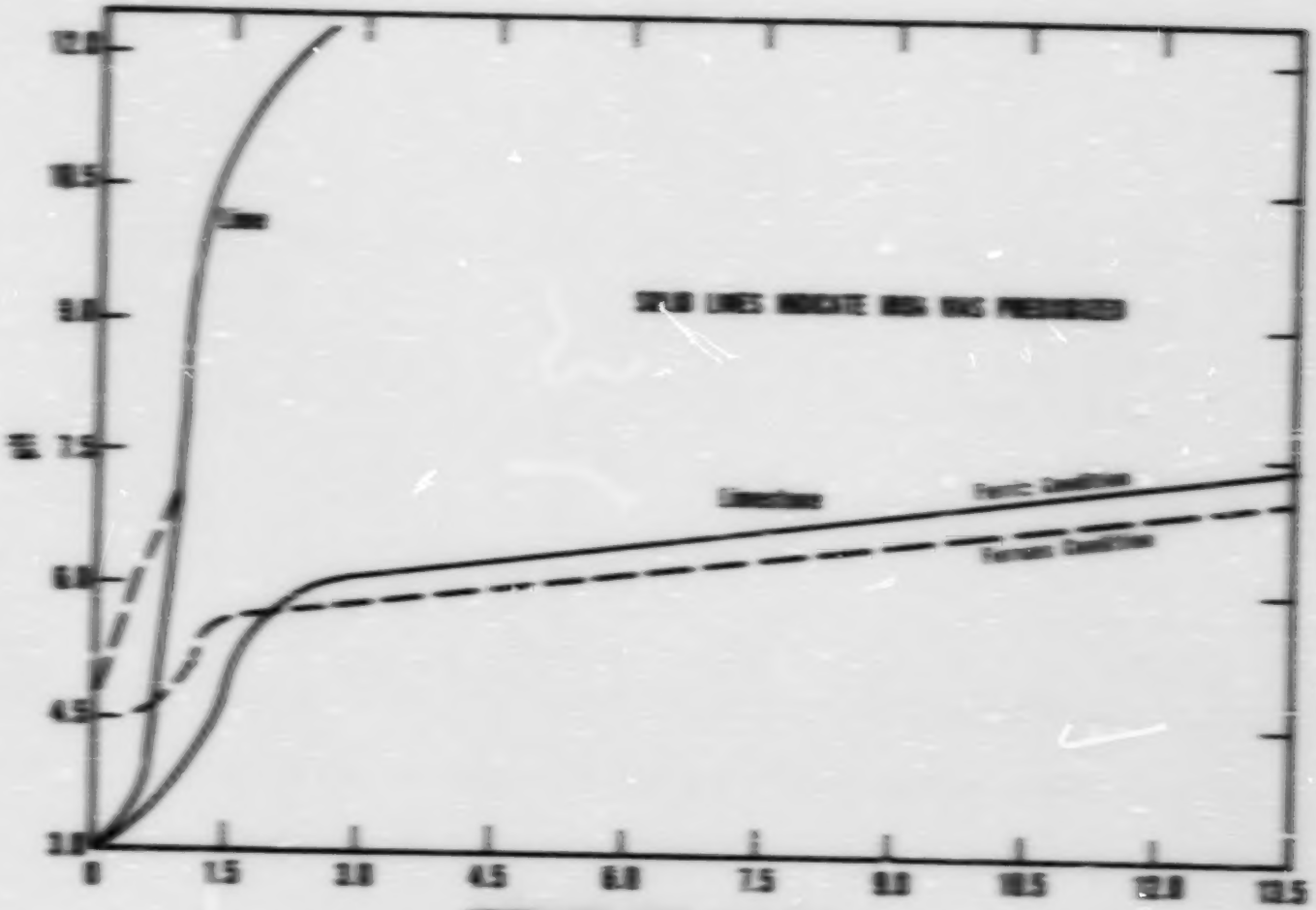


Figure 2.

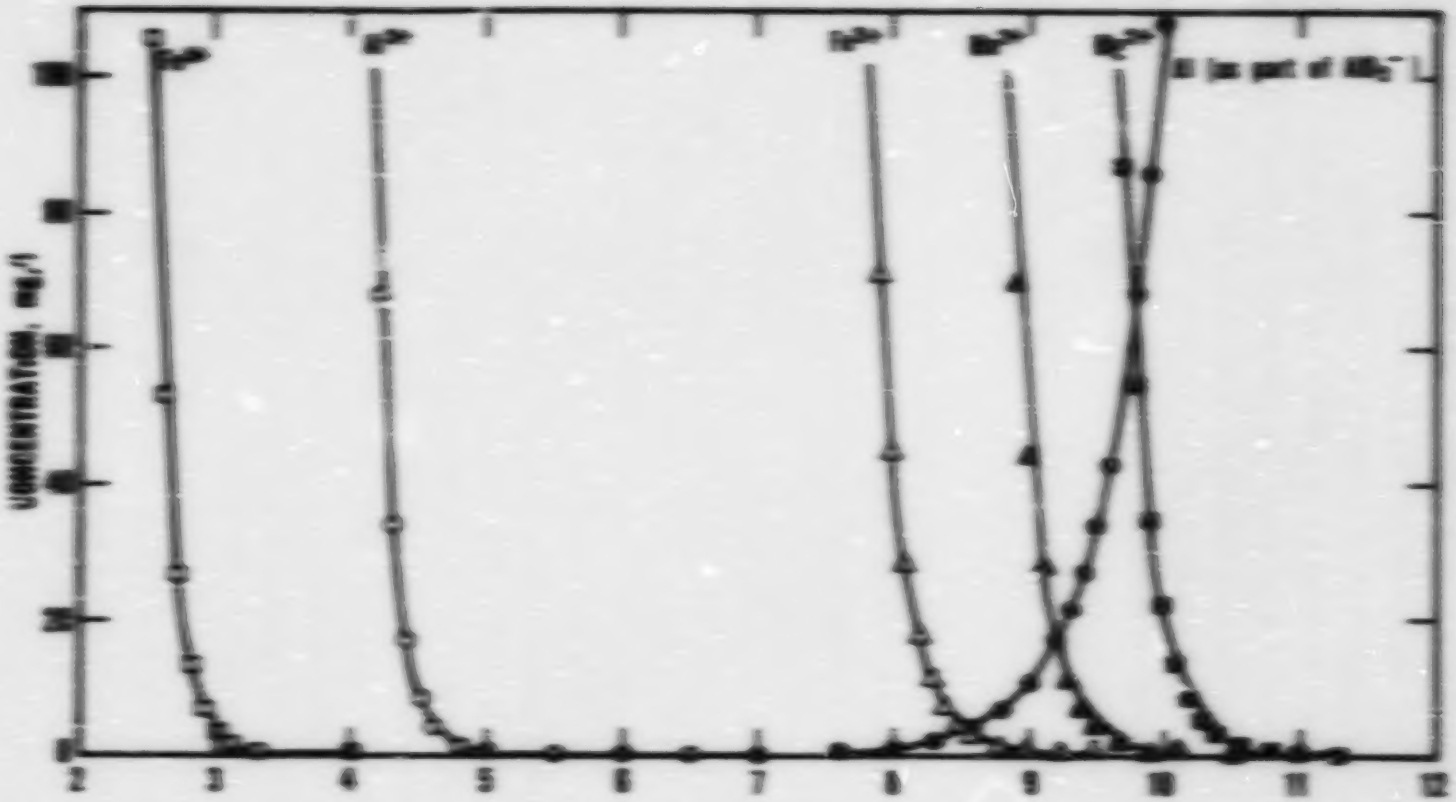


Figure 1. [illegible]

The only Ksp value not in general agreement was that for ferrous iron. The value quoted was determined by Singer, et al.,[7] and a detailed comparison with observed results is illustrated in Figure 4.

AMD samples were neutralised to various pH levels using lime, and the supernatants were analysed to determine residual concentrations. These concentrations were plotted as a function of pH in Figure 5.

Comparing the theoretical solubilities with the observed values, ferric iron precipitated approximately one-half pH unit later than predicted. Aluminum precipitated as predicted but failed to return as AlO_2^-, its amphoteric form. Ferrous iron and manganese precipitated about one and one-half pH unit sooner than predicted. Magnesium dropped out about one-half pH unit early.

Data from later continuous-flow studies in the pilot plant (Table 25) were plotted in Figure 6 to illustrate the solubilities of aluminum, manganese, magnesium, and ferric iron as a function of pH for further consideration of this topic.

The continuous-flow results agreed quite well with both the theoretical and lab studies for aluminum. As shown in the lab tests, aluminum failed to redissolve at the higher pH levels. Magnesium began to precipitate around pH 8 in the continuous-flow studies in comparison to pH 10 in the lab tests and pH 9.6 in the theoretical curves. Manganese began to precipitate at a lower pH during continuous-flow studies than in either lab studies or predicted by the theoretical curves (pH 9.5 vs pH 7 vs pH 9, respectively).

It is postulated that the deviations between the observed solubilities and the theoretical values were caused by ionic strength effects of the high TDS of the AMD and co-precipitation of these ions along with ferric hydroxide.

Ferric iron precipitation was strongly a function of the thickener hydraulics during continuous-flow studies. The ferric hydroxide floc was light and easily suspended. As a result, the ferric iron in the continuous-flow studies precipitated considerably later than in the lab tests or predicted by the theoretical curves. Filtering the continuous-flow effluent (Table 25) indicated almost complete removal of ferric hydroxide above pH 6.5. This was still much later than the lab value of pH 4 or the theoretical value of pH 3.3.

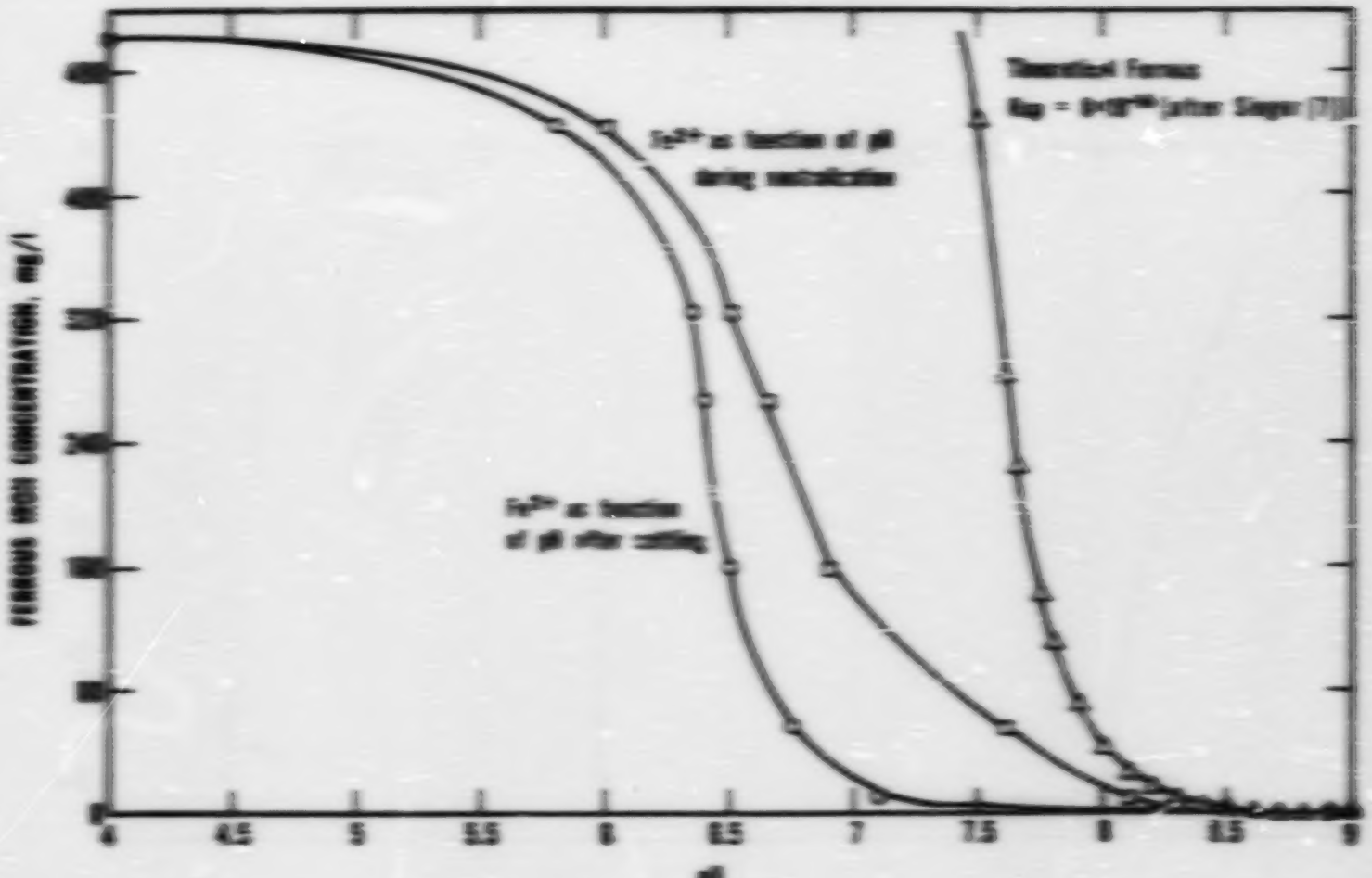


Figure 4. Effect of pH on ferrous iron stability.

CONCENTRATION, mg/l

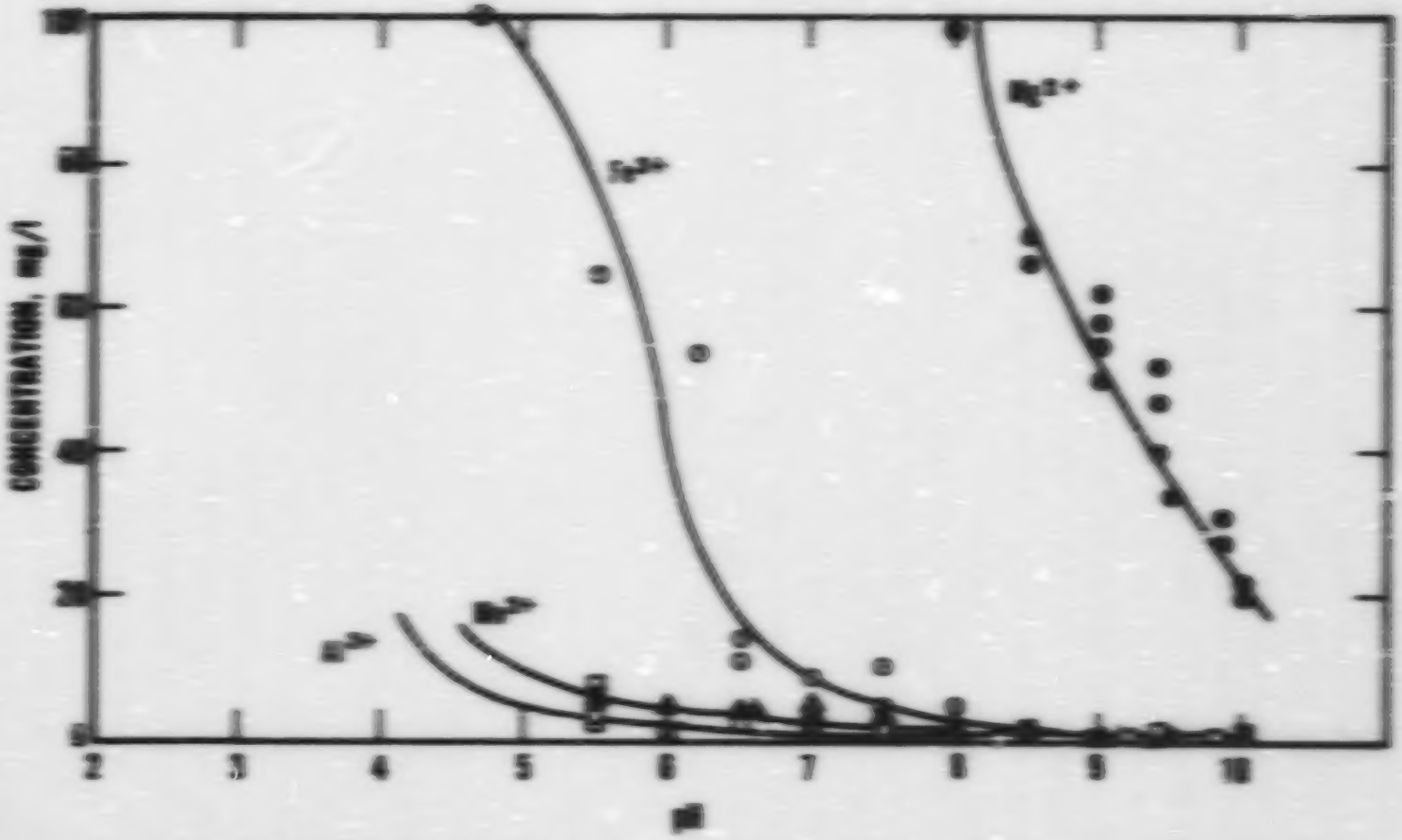


Figure 6. Observed solubility of ions as a function of treatment pH as generated from continuous-flow studies in the pilot plant.

As the continuous-flow studies incorporated some degree of oxidation, the ferrous iron parameter was of no value in this discussion. Virtually complete ferrous precipitation did occur during pH 9 studies where the ferrous iron values were reduced from 200 entering the thickener to a 1.0 mg/l effluent, as would have been expected by the theoretical curve.

BATCH-SCALE NEUTRALIZATION TESTS

A laboratory-scale study was performed to directly compare lime, limestone, and combination limestone-lime neutralization to pH 6.5 and pH 9.5. Limestone treatment was tested only at the 6.5 pH level. Since the tests were almost simultaneously conducted, results can be directly compared.

Figure 7 shows the sludge settling trends. Neutralization to pH 6.5 resulted in very-low-volume sludges because of incomplete reactions at that pH. Increasing the pH to 9.5 significantly increased sludge volumes as the iron oxidized, hydrolyzed, and precipitated. Combination-treated sludge settled more rapidly than lime sludge but the 24-hr volumes were the same. This result is not in agreement with later studies where combination sludge settled to a lesser final volume than lime sludge.

Chemical and physical data for the tests are presented in Table 7 and 8. The data in both tables are the same but are presented differently to make comparisons easier.

Very little iron oxidation occurred at pH 6.5 in 24 hr. At pH 9.5, complete oxidation occurred in a matter of minutes. Unexpectedly, very little loss in calcium and sulfate was detected by the chemical analyses.

SLUDGE CHARACTERISTICS

Bench-scale studies were made to investigate sludge characteristics as related to the neutralizing agents used and the treatment pH.

Figures 8, 9, and 10 present settling trends as a function of pH for lime, limestone, and limestone-lime treatment respectively. No clear sludge-supernatant interface developed with any of the neutralizing agents below pH 6.5. Figure 11 is a composite drawing to compare the relative settling trends of the three neutralizers at pH 7. Since the tests for each neutralizing agent were made at separate times on separate AMD samples, the direct comparison in Figure 11 is not strictly valid but may be useful as a guide. At the end of 1 hr, the limestone sludge occupied a significantly smaller volume than the other two sludges. The same situation was observed after 24 hr of settling.

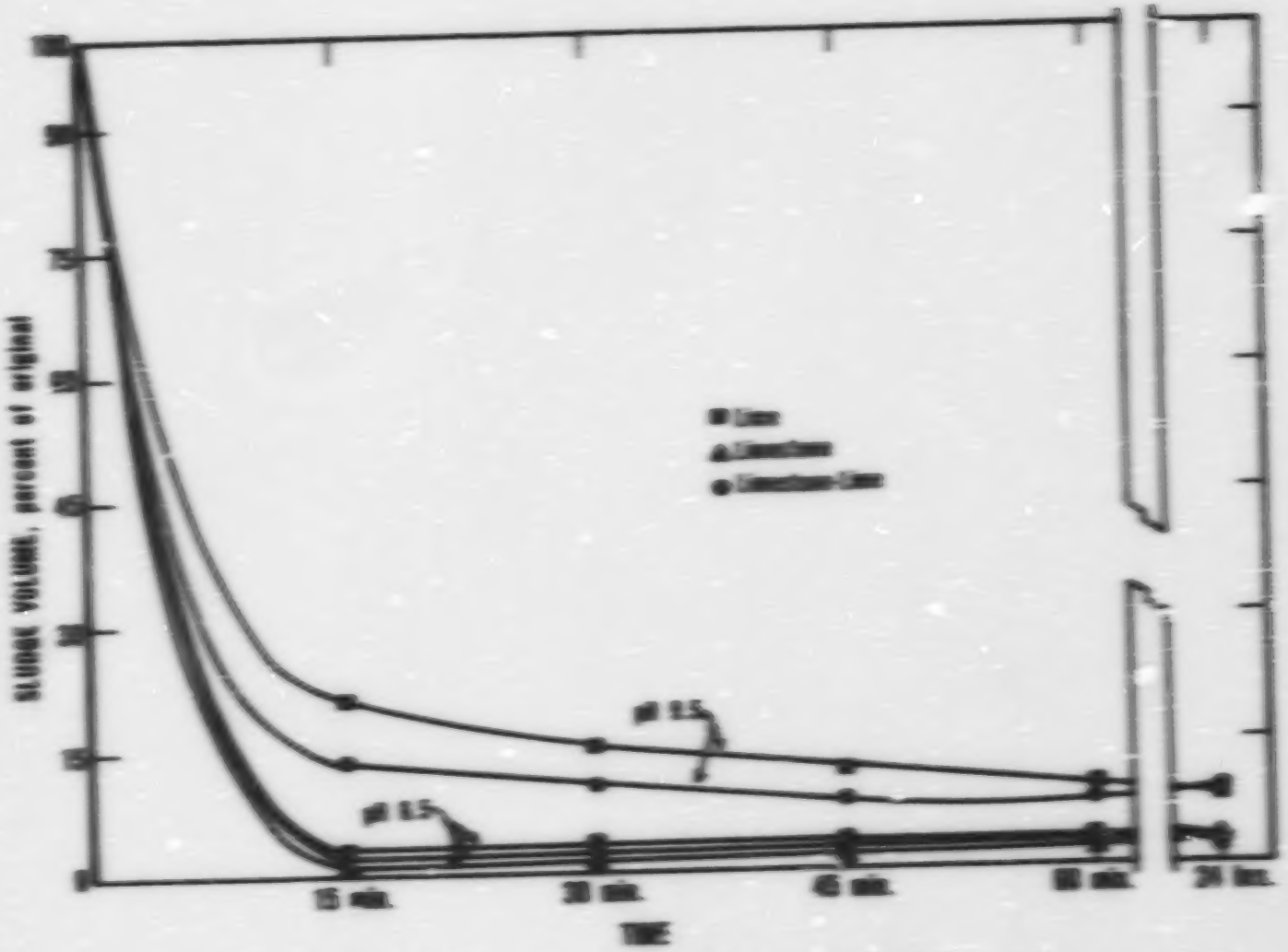


Figure 7. Comparison of settling trends at pH 6.5 and pH 8.5.

Table 7. RESULTS COMPARISON AS RELATED TO TREATMENT pH[a]

Parameter	Raw water	Lime pH 8.5	Lime pH 9.5	Limestone-lime pH 8.5	Limestone-lime pH 9.5
1-hr Settling					
Turbidity	7	62	25	60	30
Ferrous iron	930	350	0	390	0
Total iron	950	360	0.54	390	0.28
Aluminum	90	3.1	0.7	3.2	0.9
Manganese	9.2	11	0.51	12	0.37
Magnesium	180	200	150	200	150
Calcium	450	790	1020	740	1010
Sodium	620	640	610	620	610
Sulfate	4030	3780	3690	3900	3900
Conductivity	4800	5200	5050	4900	4950
Acidity	1450	---	0	760	0
Alkalinity	0	---	---	---	---
Sludge % solids		1.6	6.9	4.4	9.3
24-hr Settling					
Turbidity	7	14	6	42	7
Ferrous iron	930	140	0	380	0
Total iron	950	140	0.07	380	0.09
Aluminum	90	1.1	0.9	1.2	1.0
Manganese	9.2	11	0.19	12	0.26
Magnesium	180	180	130	180	130
Calcium	490	730	1010	730	1050
Sodium	620	600	590	590	590
Sulfate	4050	3940	3690	3940	3900
Conductivity	4800	4750	5000	4950	5100
Acidity	1450	717	0	780	0
Alkalinity	0	5	79	5	81
Sludge % solids		9.2	6.9	4.3	6.1

[a]All units are mg/l except for turbidity (JTU) and sludge percent solids.

Table 6. RESULTS COMPARISON AS RELATED TO SETTLING TIME[a]

Parameter	Raw water	Lime		Limestone		Combination	
		1-hr	24-hr	1-hr	24-hr	1-hr	24-hr
At pH 6.5							
Turbidity	7	62	34	190	49	80	42
Ferrous iron	530	350	340	470	450	390	330
Total iron	550	360	340	490	450	390	380
Aluminum	50	3.1	1.1	3.7	1.3	3.0	1.0
Manganese	9.0	11	11	12	12	12	12
Magnesium	160	200	180	200	190	200	180
Calcium	450	790	720	710	640	740	730
Sodium	590	640	600	630	575	620	590
Sulfate	4050	3760	3940	3940	3760	3900	3940
Conductivity	4800	5200	4750	5100	4950	4900	4950
Acidity	1450	--	717	950	940	760	780
Alkalinity	0	--	0	--	0	--	5
Sludge % solids		3.6	5.0	4.5	6.7	4.4	4.3
At pH 9.5							
Turbidity	7	85	6	---[b]	---[b]	30	7
Ferrous iron	530	0	0	---	---	0	0
Total iron	550	0.94	0.67	---	---	0.88	0.09
Aluminum	50	0.7	0.9	---	---	0.9	1.0
Manganese	9.0	0.31	0.19	---	---	0.37	0.06
Magnesium	160	190	130	---	---	190	130
Calcium	450	1020	1010	---	---	1010	1050
Sodium	590	610	590	---	---	610	590
Sulfate	4050	3690	3690	---	---	3900	3900
Conductivity	4800	5050	5000	---	---	4950	5100
Acidity	1450	0	0	---	---	0	0
Alkalinity	0	--	79	---	---	--	81
Sludge % solids		6.5	6.5	---	---	9.3	6.1

[a]All units are mg/l except for turbidity (JTU) and sludge percent solids.

[b]Not applicable.

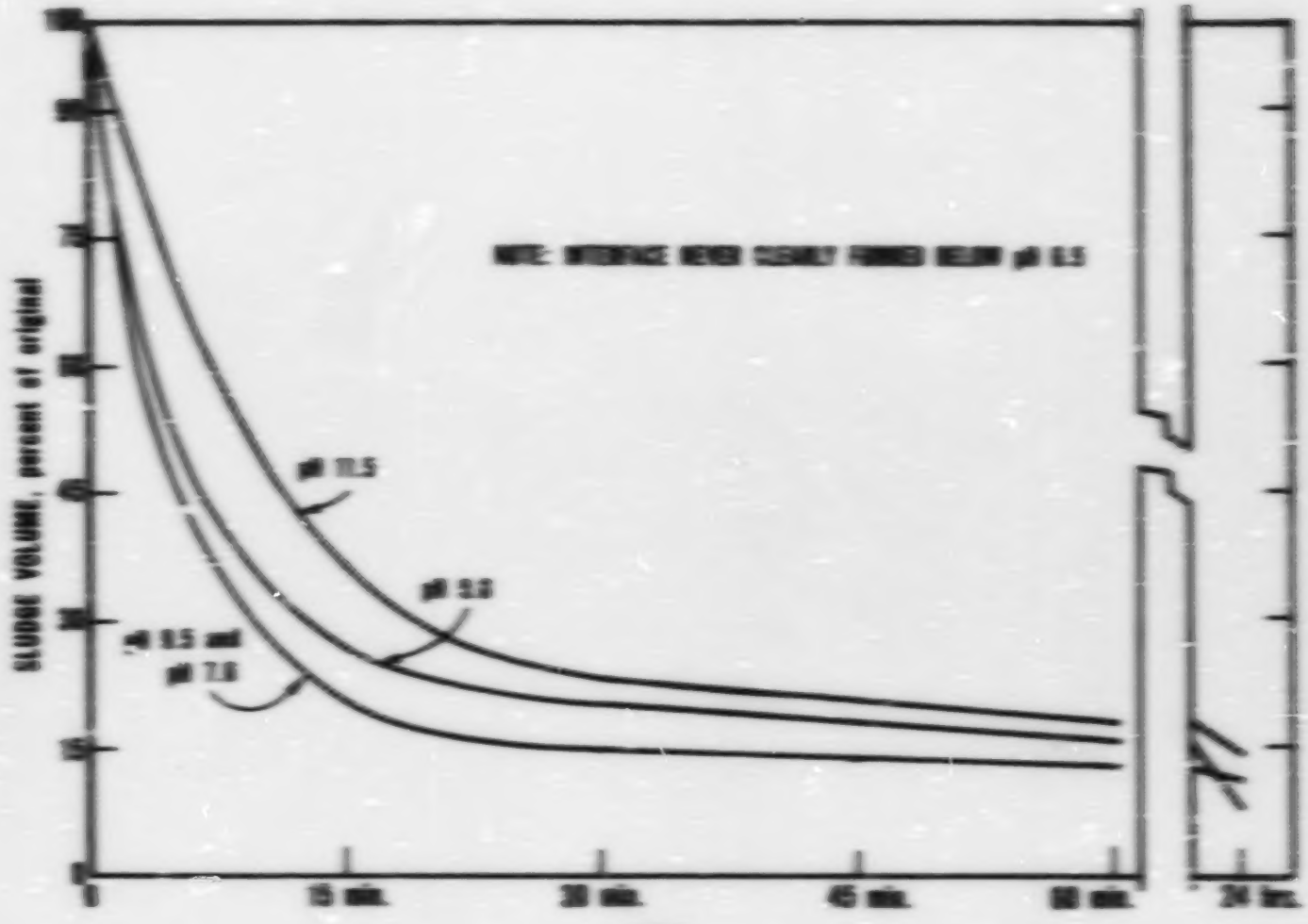


Figure 8. Settling tests for lime neutralization.

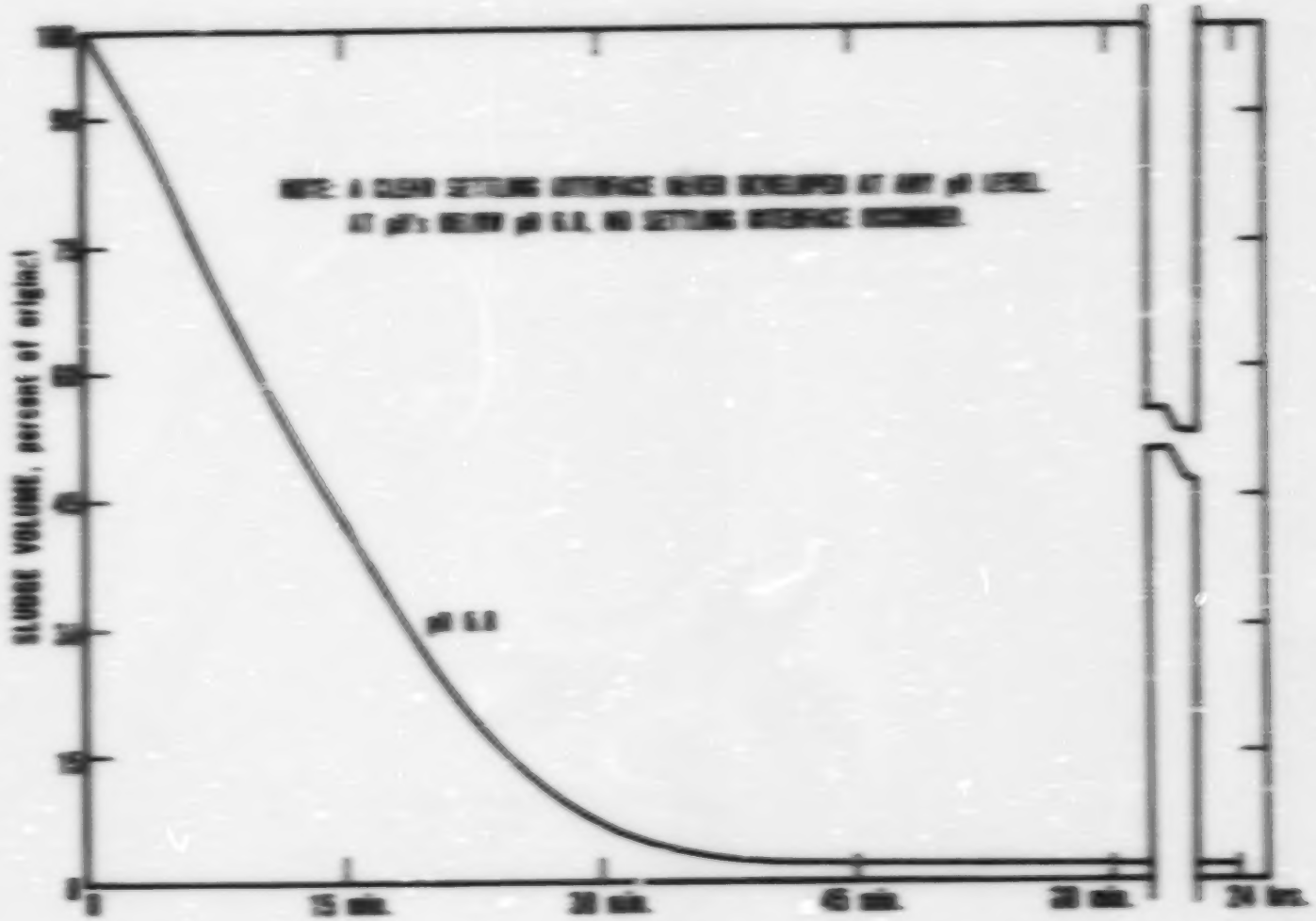
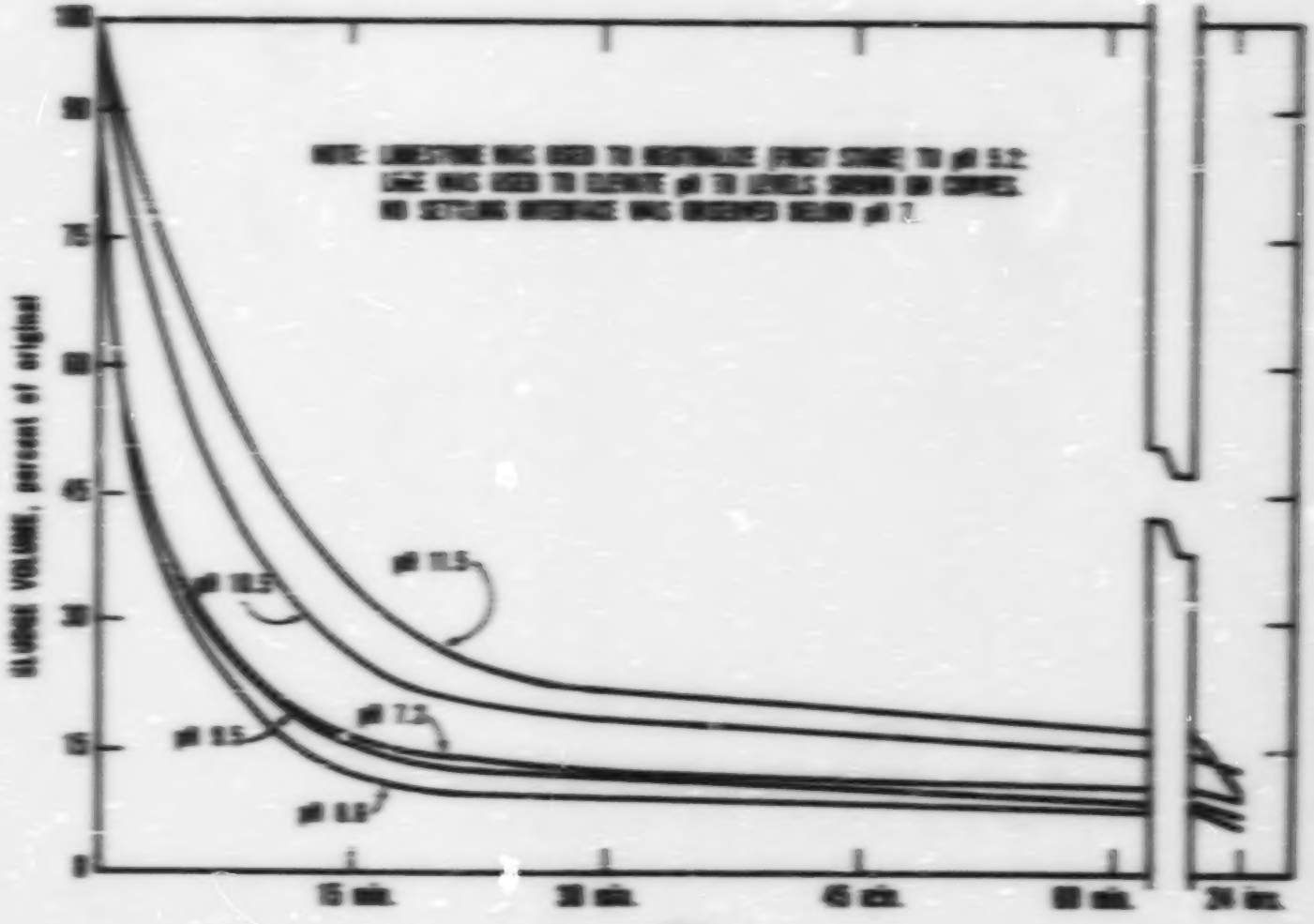
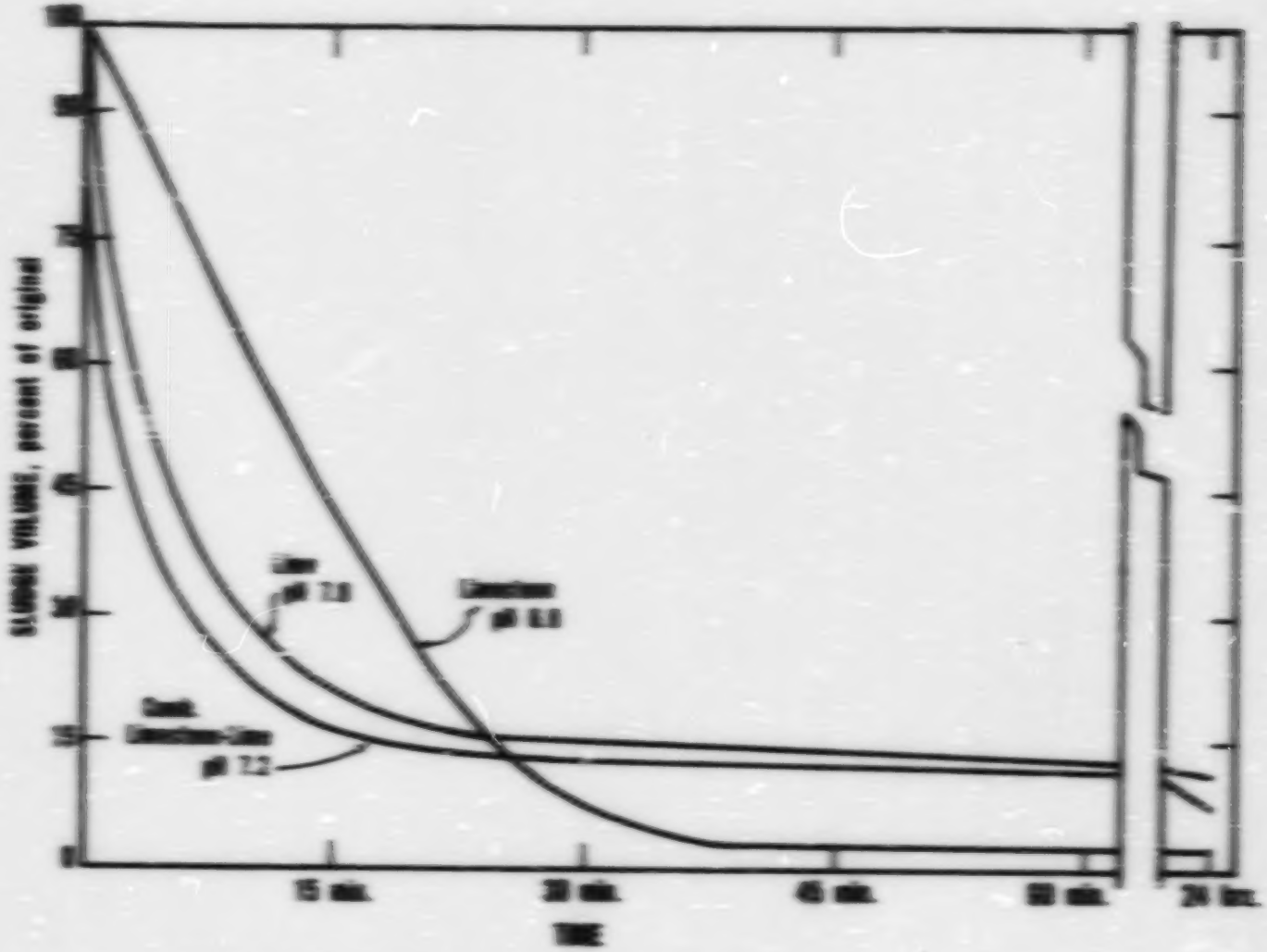


Figure 8. Settling trends for limestone neutralization.




15 min.
30 min.
45 min.
60 min.
24 hrs.

Effluent turbidity and sludge percent-solids determinations were made on each sample after 1 hr and after 24 hr of settling. The results are shown in Figures 12 through 15. Limestone effluent turbidity, after 1 hr was high in comparison to lime and to combination treatment. At pH 6.8, limestone sludge had a percent-solids content about four times as great as the other two sludges.

Surprisingly, little change occurred in the sludge percent-solids between the 1-hr and 24-hr times in all the samples. Supernatant turbidity values were significantly lower for all samples after 24 hr of settling as compared to the 1-hr values.

In summary, limestone sludge settled fastest and compacted to the least volume. Supernatant clarity from limestone treatment was poor, however, in relation to lime treatment and combination treatment. Combination limestone-lime sludge settled more rapidly than lime and settled to a final volume, which was on the order of one-half that of lime-generated sludge at pH 7. Supernatant clarity from combination treatment after 24 hr was superior to that from lime treatment.

REAGENT COSTS FOR BATCH NEUTRALIZATION

Bench-scale tests were made to determine the feasibility of combination limestone-lime treatment of the Crown AMD. One-liter samples were neutralized to various predetermined pH's with limestone, allowing 30-min reaction time, and then were treated with lime to pH 7.0 and further to pH 9.5 (for ferrous oxidation or precipitation). The quantities of limestone and lime were recorded. For comparison, samples were treated to pH 7.0 using limestone alone. Lime was used alone to treat to pH 7.0 and pH 9.5.

The important consideration in this test was cost. Raw material costs at Crown were: Limestone = $12.13 per tonne in bulk, and lime = $30.98 per tonne. Table 9 and Figure 16 contain the data from the feasibility test. Combination treatment using a first-stage limestone pH of 5.1 was the most economical method of treating to pH 7.0. This combination (1.7 cents/cu m) was 57 percent cheaper than straight limestone treatment (3.9 cents/cu m) and 9 percent cheaper than straight lime treatment (1.8 cents/cu m).

Treatment to pH 9.5 was most economical using combination treatment with a first-stage limestone pH of 5.5. In this case, combination treatment (3.5

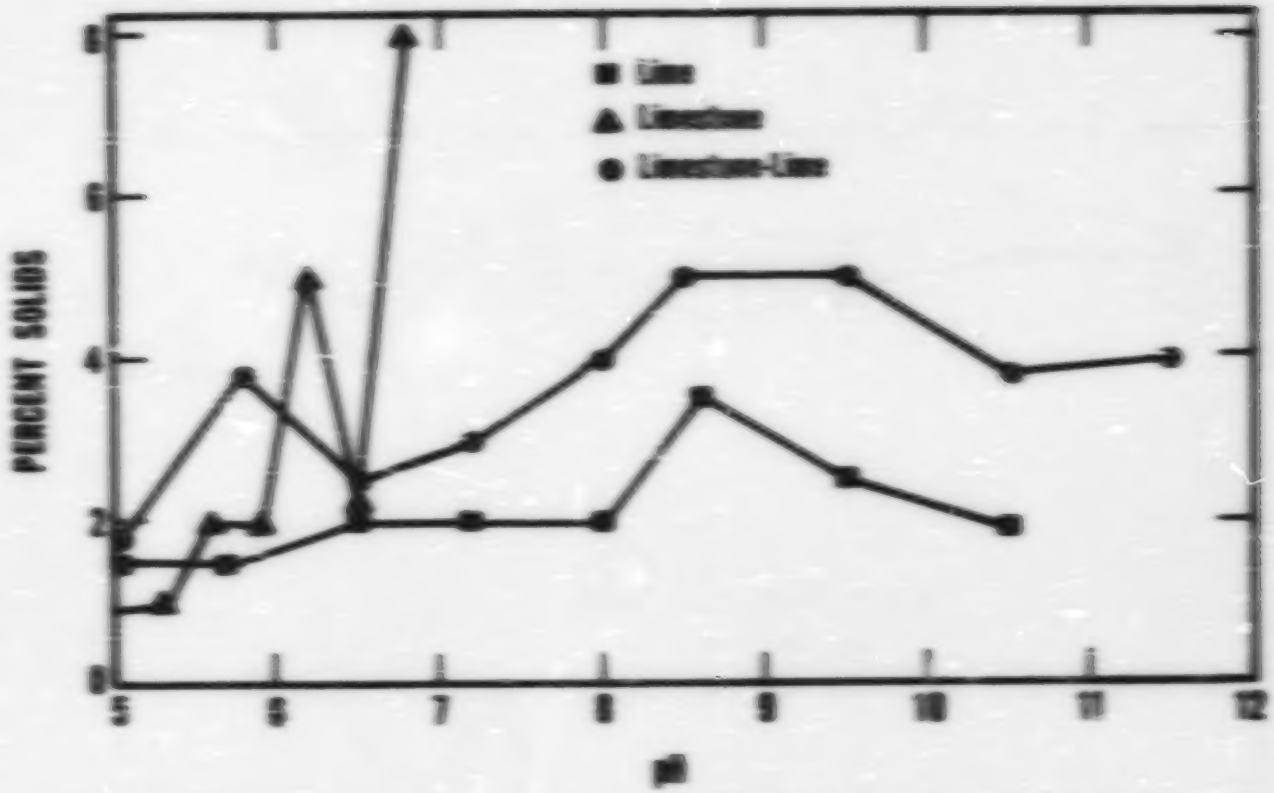


Figure 12. Sludge percent solids @ 1-hr. settling time as a function of pH.

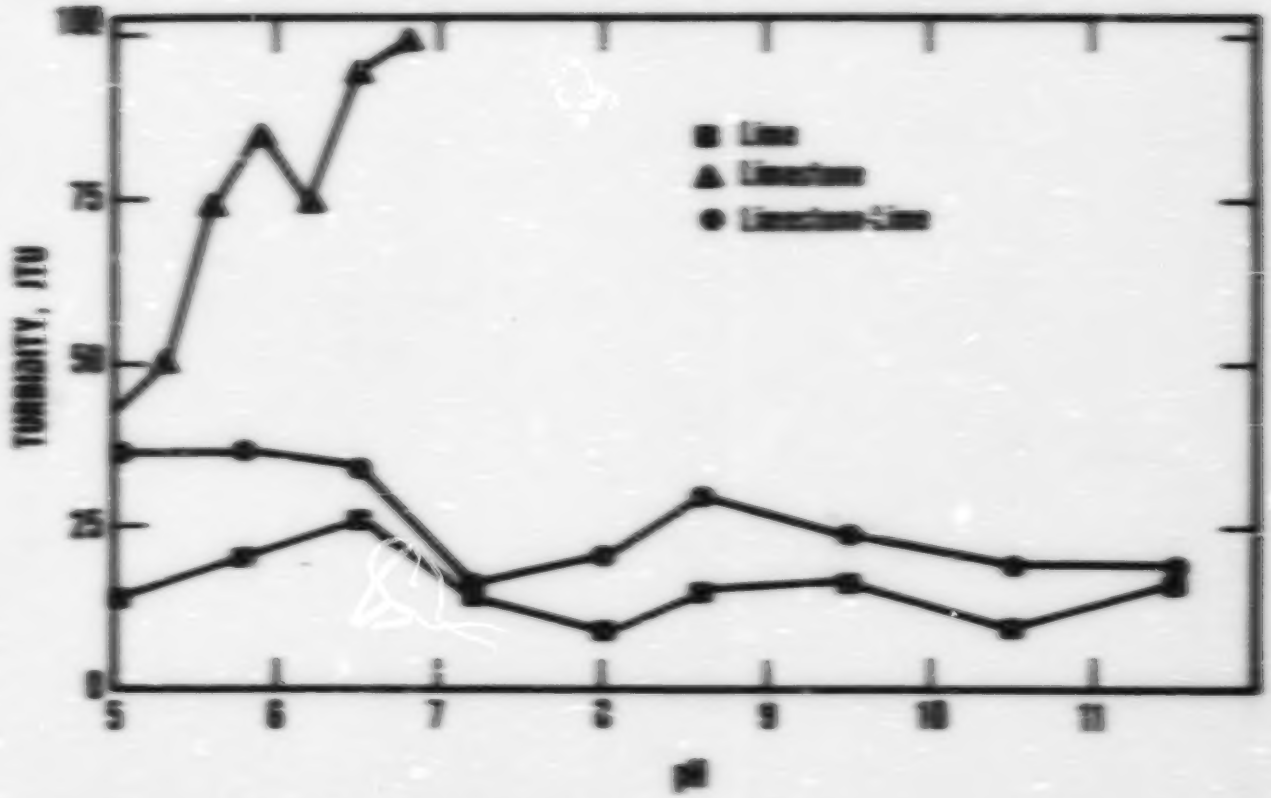


Figure 13. Supernatant turbidity @ 1-hr. settling time as a function of pH.

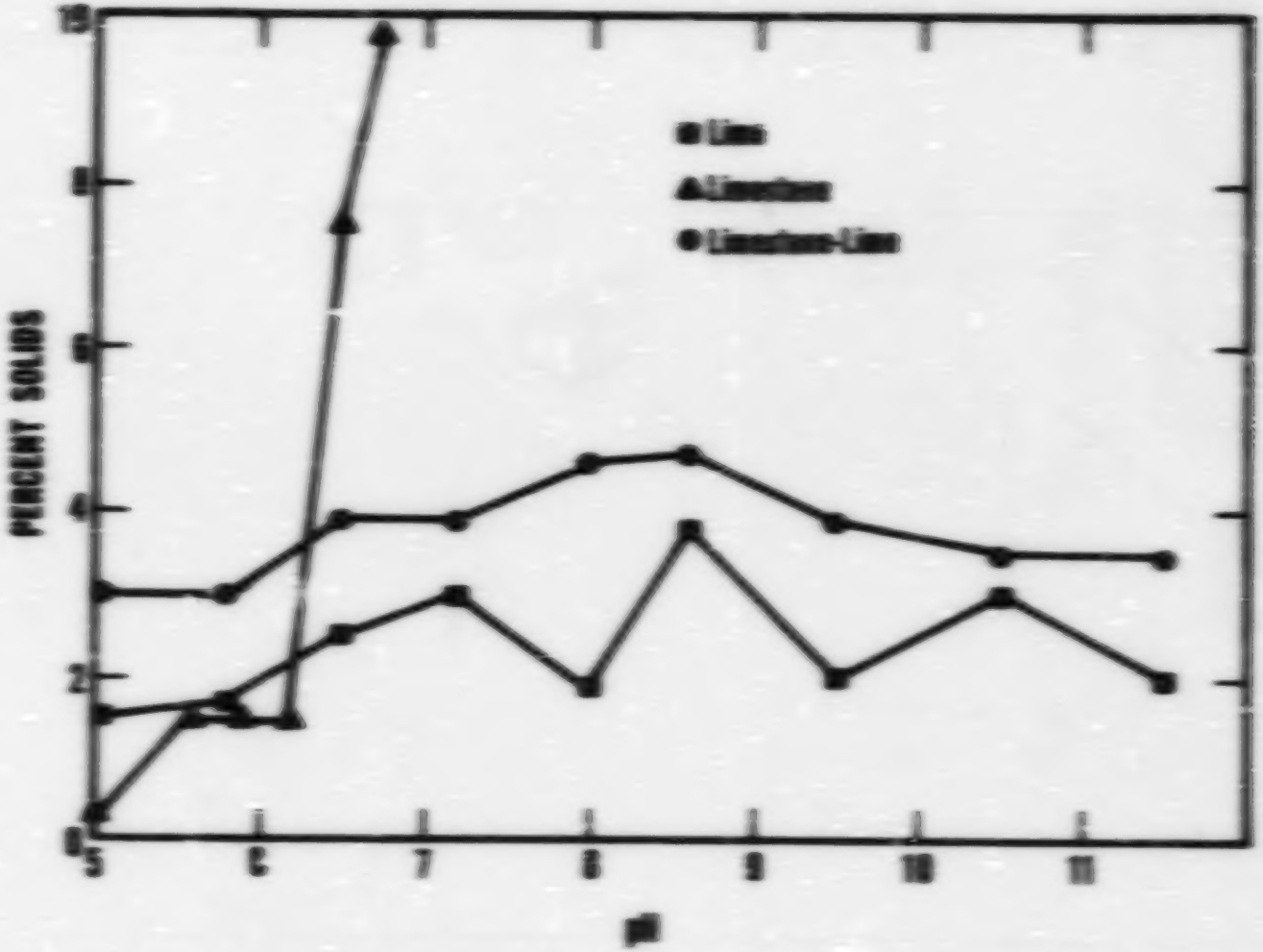


Figure 14. Sludge percent solids @ 24-hr. settling time as a function of pH.

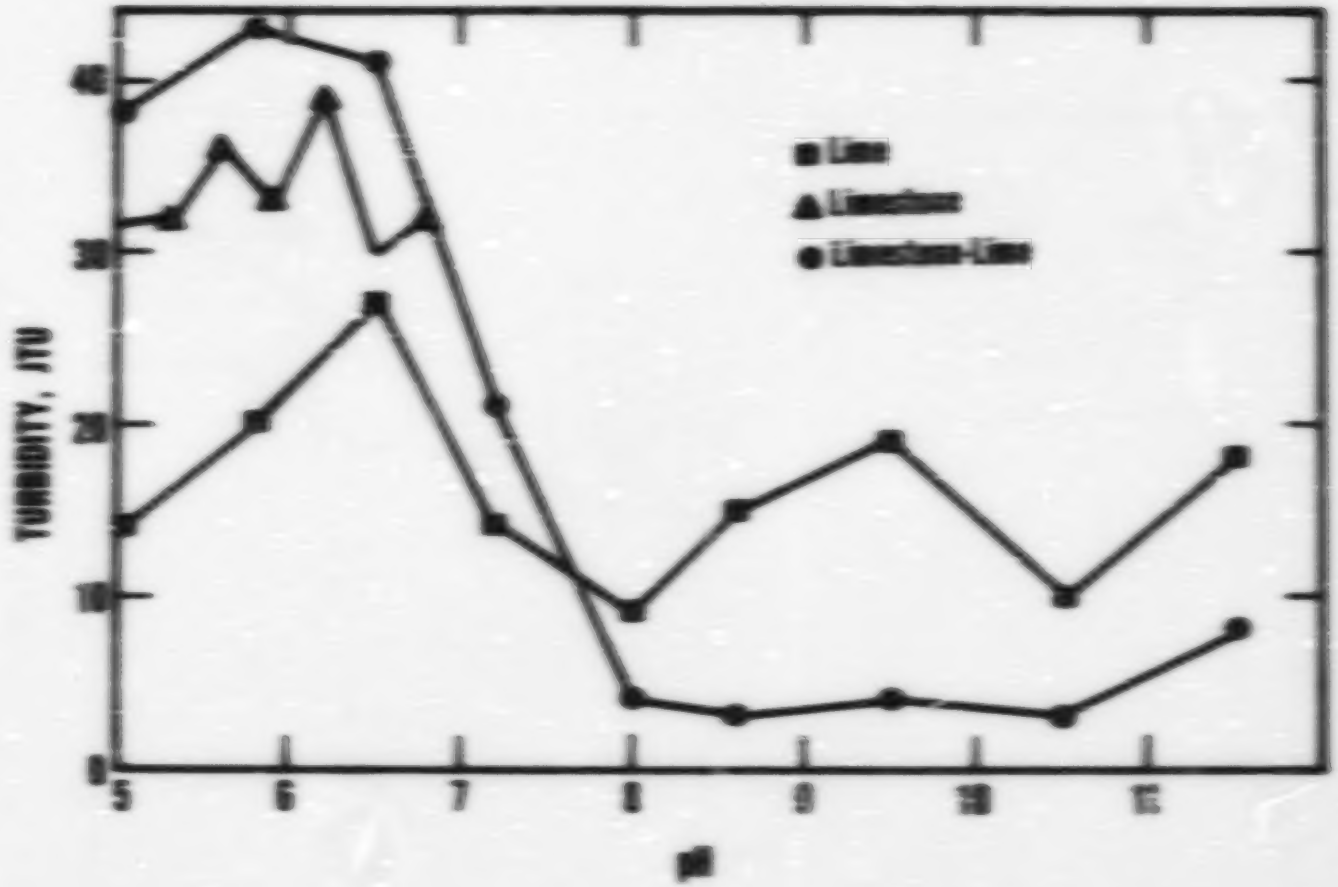


Figure 15. Supernatant turbidity @ 24-hr. settling time as a function of pH.

Table 5. [illegible][a]

Treatment	Limestone			Lime		Total cost to pH 7.0, dlrs a	Lime		Total cost to pH 9.5, dlrs a
	Final stage pH	Amount, g/l	Cost,[b] dlrs a	Amt. to pH 7., g/l	Cost, dlrs a		Amt. to pH 9.5, g/l	Cost, dlrs a	
[illegible]	6.8	3.2500	3.917			3.917			
Lime				0.4820	1.550	1.550	0.8950	3.195	3.195
Combination	5.1	0.0246	1.029	0.4310	1.463	1.492	0.6950	2.621	2.710
"	5.3	0.0930	0.101	0.4410	1.701	1.802	0.6660	2.570	2.671
"	5.5	0.1160	0.143	0.4380	1.690	1.833	0.6810	2.319	2.462
"	5.7	0.1500	0.182	0.4800	1.852	2.034	0.7380	2.847	3.029
"	5.9	0.1730	0.210	0.4780	1.844	2.054	0.6980	2.693	2.903
"	6.1	0.1910	0.232	0.4130	1.593	1.825	0.7230	2.771	2.903
"	6.3	0.4020	0.487	0.4110	1.586	2.073	0.7690	2.967	3.454

[a]Raw water pH = 5.0. Raw material cost: lime, $58.38/tonne; limestone, $12.13/tonne.

[b]To convert from cents/m a to cents/1000 gal, multiply by 3.785.

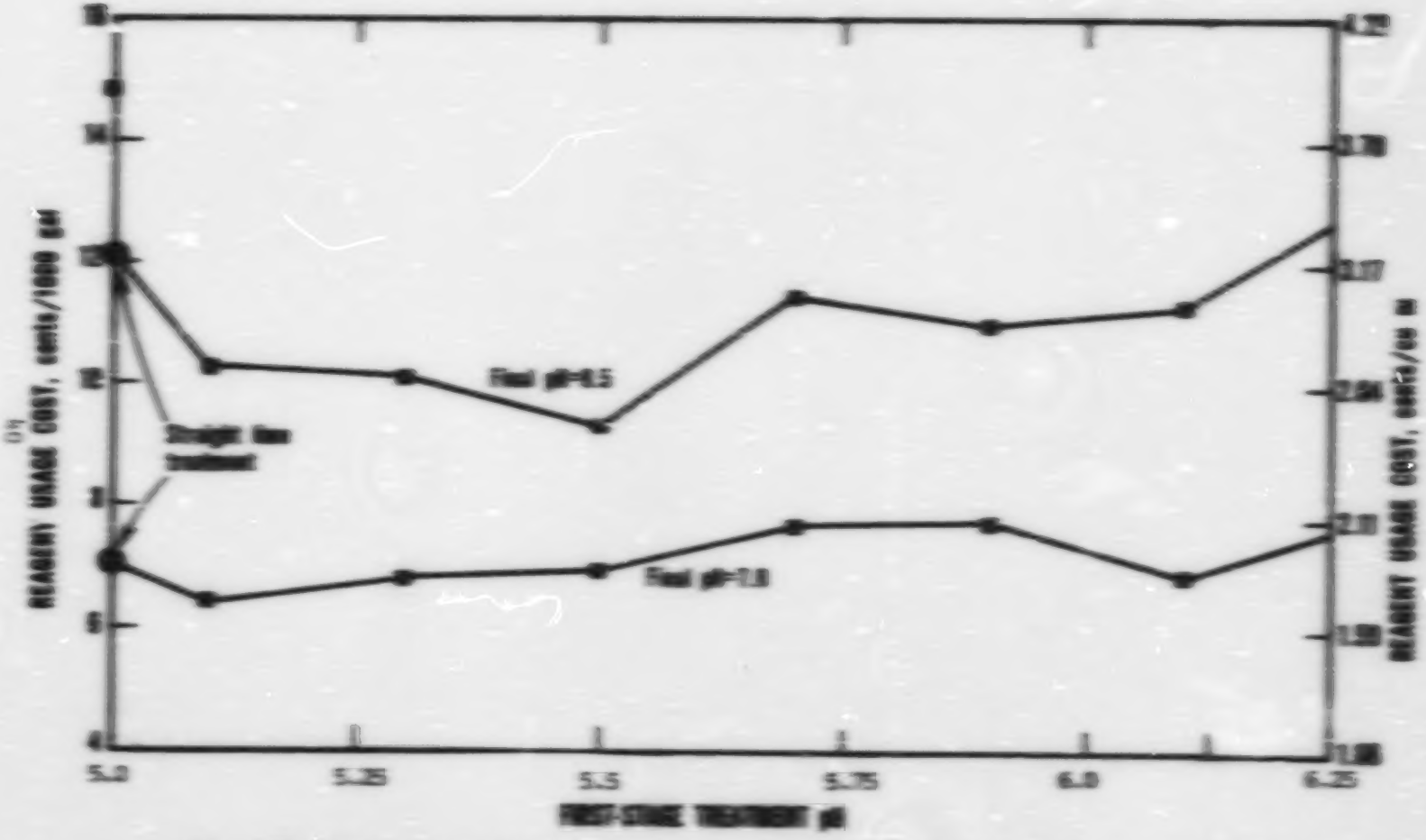


Figure 35. Batch-scale coagulation-flocculation-sedimentation tests with raw water pH was 5.0.

cents/cu m) was 21-percent cheaper than straight lime treatment to pH 9.5 (3.8 cents/cu m). Limestone was incapable of treating to pH 9.5.

The raw materials costs greatly influence the cost advantage of combination treatment. Any consideration of combination treatment would need to include the delivered cost of bulk lime and rock dust for the plant site in question.

FULL-SCALE, CONTINUOUS-FLOW STUDIES ON LIMESTONE NEUTRALIZATION

Introduction

The basis for these studies (i.e., pH, detention time, reagent addition mode, reactor baffling system, etc.) was the earlier investigation by MPA[1] on the ferric iron AMD at Morton, West Virginia. In this earlier study, it was determined that 20 to 30 min of detention time was required in the mixing reactor, that wire-mesh reactor baffles increased efficiency, and that the rock-dust form of limestone yielded utilization efficiencies in the range of 90 percent with treatment to pH 6.5.

The current MPA facility provided 40 min of reaction time in the limestone reactor at 1 liter/sec (16 gpm). Approximately 2 hr of detention time was provided in the aerator (at 1 liter/sec) and approximately 10 hr of settling time was available in the thickener.

Cost figures for limestone requirements are based upon $10.13/tonne ($11.00/ton).

The limestone investigations basically followed the research plan outlined in Table 10.

Test One - Basic Data

Basic data for the limestone neutralization process were generated utilizing both Processes A and B operating at pH 6.5 and 1 liter/sec (16 gpm). Operating parameters are detailed in Table 11 and chemical data (from all the limestone studies) are presented in Table 12. Utilization efficiencies were very low (25 percent) and effluent qualities were poor (total iron, 180 mg/l; ferrous iron, 110 mg/l). These efficiencies were well below observed values from previous studies on ferric iron AMD.[1]

Test Two - Additional Mixing and Longer Detention Times

To investigate the possibility that insufficient mixing was responsible for the low utilization efficiencies, Process B utilized two reactors in series. To increase detention times, the flow rates in both processes were

Table 10. RESEARCH PLAN FOR LIMESTONE INVESTIGATIONS

Order of study	Variable	Action investigated
1	None	Basic data, pH 6.5, 1 liter/sec
2	Extra mixing	Effect upon efficiency
3	H_2SO_4 injection	Effect upon efficiency
4	Detention time	Effect upon efficiency
5	Preoxidation of iron	Effect upon efficiency
6	Sludge recycle	Effect upon efficiency
7	Recycle rate	Effect upon efficiency
8	Aeration detention time	Effect upon effluent iron levels
9	Aeration detention time	Effect upon effluent iron levels
10	Coagulant addition	Effect upon effluent iron levels
11	Coagulant addition and detention time	Effect upon effluent iron levels

Table 11. NEUTRALISATION DATA SUMMARIES FOR LIMESTONE @ pH 6.5 AND 1 LITER/SEC

		Mean	Std. Dev.
Effluent pH	A	6.44	0.05
	B	6.50	0.04
Neutraliser usage, kg/cu m	A	1.70	0.0
	B	1.75	0.0
Neutraliser usage, lbs/1000 gal	A	13.4	1.4
	B	14.6	1.0
Neutraliser usage, g/cu m/ppm influent acidity	A	2.54	0.0
	B	2.60	0.0
Cost, cents/1000 gal	A	7.29	0.0
	B	8.03	0.7
Cost, cents/cu m	A	1.93	0.0
	B	2.12	0.0
Cost, cents/10^3cu m/ppm influent acidity	A	3.06	0.0
	B	3.40	0.0
Utilisation efficiency, percent	A	27	1.6
	B	25	3.4
Stoichiometric factor (influent acidity)	A	2.54	0.0
	B	2.60	0.0
Sludge to waste, % of influent AMD	A	3.0	0.3
	B	3.0	0.0
Dry solids to waste, lbs/1000 gal	A	6.4	0.7
	B	9.4	16.9
Dry solids to waste, kg/cu m	A	0.77	1.1
	B	1.13	2.0
Underflow solids, percent	A	2.0	0.7
	B	1.7	6.5
Effluent turbidity, JTU	A	50	12
	B	50	11
Difference in reagent usage between Process A and B, percent		10.0	

| | | |

[illegible]

[illegible]

[illegible]

[illegible]

| [illegible] | [illegible] | [illegible] |

lowered from 1 liter/sec to 0.5 liter/sec (8 gpm). Results (Table 13) of the study indicated that no difference in efficiency occurred from using two reactors in series as compared to a single reactor; however, the increase in detention time resulted in efficiencies of 50 percent as contrasted with the 25-percent values at Test One's 1-liter/sec flow rate. Effluent iron values were significantly improved (50 mg/l), although far from satisfactory. This increase in efficiency was later found to be in error and was postulated to have been caused by the failure of the limestone supplier to adequately clean the bulk truck of lime or quicklime prior to loading the rock dust. Consequently, spikes of high efficiency occurred during the week of data collection. This variance is illustrated by the standard deviation values for the efficiency (Table 13).

Test Three - Sulfuric Acid Injection

It was felt that the reaction of limestone would be more efficient if the influent pH were lower than the pH 5 values of the Crown water. Since more free acidity would be available at the lower pH, the probability of acid-base collision and interaction would be much greater and the reaction should be more efficient. To test this theory, sulfuric acid was injected into Process B to lower the influent pH from 5.4 to 3.4. Flow rates were returned to 1 liter/sec (15.8 gpm) for both processes. Contrary to expectations, results of the study (Table 14) indicated no significant difference in efficiency because of influent pH. Even more disturbing was the fact that efficiencies had fallen again to the 20-percent range. Effluent qualities were still poor (Table 12).

Test Four - Detention Time

Since the 0.5 liter/sec test (Test Two) had indicated an apparently higher efficiency, the effect of flow rate was directly compared by operating Process A at 1 liter/sec and Process B at 0.5 liter/sec. The study indicated no significant difference could be gained by operating at the lower flow rate (Table 15). In fact, the lower flow-rate condition had a lower utilization efficiency than the 1-liter/sec process. This was attributed to the slightly higher effluent pH of Process B (6.48 vs 6.58). Advantages were noted in iron oxidation (Table 12) where the effluent ferrous iron values of Process B were 81 mg/l as compared to 200 mg/l for Process A. Turbidities were about

Table 13. NEUTRALISATION DATA SUMMARISED FOR LIMESTONE @ 0.5 LITRE/CUBIC METRE PROCESS B UTILISED AN ADDITIONAL REACTOR FOR MIXING

	Process	Mean	Std. Dev.
Effluent pH	A	6.48	0.03
	B	6.50	0.03
Neutraliser usage, kg/cu m	A	1.16	0.9
	B	1.18	0.9
Neutraliser usage, lbs/1000 gal	A	9.7	4.1
	B	9.9	3.8
Neutraliser usage, g/cu m/ppm influent acidity	A	1.80	0.8
	B	1.84	0.7
Cost, cents/1000 gal	A	5.33	2.3
	B	5.40	2.1
Cost, cents/cu m	A	1.41	0.6
	B	1.43	0.6
Cost, cents/10^3cu m/ppm influent acidity	A	2.19	0.9
	B	2.23	0.9
Utilisation efficiency, percent	A	55	16
	B	53	19
Stoichiometric factor (influent acidity)	A	1.80	0.8
	B	1.84	0.7
Sludge to waste, % of influent AMD	A	6.1	0.4
	B	5.4	0.2
Dry solids to waste, lbs/1000 gal	A	3.6	0.6
	B	6.5	7.7
Dry solids to waste, kg/cu m	A	0.43	0.1
	B	0.78	0.9
Underflow solids, percent	A	0.69	0.1
	B	1.45	1.7
Effluent turbidity, JTU	A	48	14
	B	47	1.9
Difference in reagent usage between Process A and B, percent		1.9	

Table 14. NEUTRALIZATION DATA SUMMARIES FOR LIMESTONE @ 1 LITER/MIN WHERE H_2SO_4 WAS INJECTED INTO PROCESS B TO LOWER INFLUENT pH FROM 5.6 TO 3.4

	Process	Mean	Std. Dev.
Effluent pH	A	6.50	0.07
	B	6.49	0.06
Neutraliser usage, kg/cu m	A	2.87	0.6
	B	3.88	0.7
Neutraliser usage, lbs/1000 gal	A	23.9	5.4
	B	32.4	6.0
Neutraliser usage, g/cu m/ppm influent acidity	A	5.65	1.2
	B	5.83	1.4
Cost, cents/1000 gal	A	13.16	3.5
	B	17.82	3.3
Cost, cents/cu m	A	3.48	0.9
	B	4.71	0.9
Cost, cents/10^3cu m/ppm influent acidity	A	6.85	2.3
	B	7.07	1.7
Utilization efficiency, percent	A	16	4.9
	B	17	4.0
Stoichiometric factor (influent acidity)	A	5.7	1.2
	B	5.8	1.4
Sludge to waste, % of influent AMD	A	3.1	0.5
	B	2.6	0.2
Dry solids to waste, lbs/1000 gal	A	22.6	8.5
	B	22.6	71
Dry solids to waste, kg/cu m	A	2.71	1.0
	B	2.71	1.3
Underflow solids, percent	A	8.7	3.2
	B	10.7	5.4
Effluent turbidity, JTU	A	10	9
	B	61	12
Effluent suspended solids, mg/l	A	70	12
	B	80	18

Table 15. NEUTRALISATION DATA SUMMARIES FOR LIMESTONE @ 1 LITER/SEC (PROCESS A) COMPARED TO 0.5 LITER/SEC (PROCESS B)

	Process	Mean	Std. Dev.
Effluent pH	A	6.58	0.03
	B	6.58	0.08
Neutraliser usage, kg/cu m	A	1.90	0.4
	B	1.70	0.9
Neutraliser usage, lbs/1000 gal	A	15.7	6.9
	B	11.0	7.2
Neutraliser usage, g/cu m/ppm influent acidity	A	6.88	1.2
	B	5.75	1.5
Cost, cents/1000 gal	A	8.66	3.8
	B	17.06	5.0
Cost, cents/cu m	A	2.29	1.0
	B	4.51	1.7
Cost, cents/10^3cu m/ppm influent acidity	A	3.49	1.3
	B	6.97	1.8
Utilisation efficiency, percent	A	81	7.8
	B	19	3.9
Stoichiometric factor (influent acidity)	A	2.9	1.2
	B	5.8	1.5
Sludge to waste, % of influent AMD	A	3.6	0.3
	B	4.3	1.0
Dry solids to waste, lbs/1000 gal	A	15.5	12
	B	19.5	6.8
Dry solids to waste, kg/cu m	A	1.86	1.4
	B	2.33	0.7
Underflow solids, percent	A	5.0	4.4
	B	5.4	1.0
Effluent turbidity, JTU	A	68	17
	B	60	10
Effluent suspended solids, mg/l	A	70	30
	B	56	19
Difference in reagent usage between Process A and B, percent		97	

equal on both processes, but the effluent suspended solids were somewhat lower on Process B. Overall effluent qualities were still poor.

Test Five - Preoxidation of Iron

Since the discrepancy in efficiency values between earlier[1] results on ferric iron AMD and the current studies had still not been resolved, it was decided to directly compare ferrous vs ferric by oxidising the iron in Process B prior to entering the limestone reactor. This preoxidation was accomplished by injecting hydrogen peroxide (H_2O_2) into the influent piping of Process B and modifying the piping arrangement to facilitate in-line mixing. A Precision Model 1232i-11 diaphragm-type chemical pump was used to inject the H_2O_2 in-line. AMD flows in both processes were 1 liter/sec (16 gpm).

An average addition rate of 35-percent H_2O_2 during the study was 0.0007 ml H_2O_2/cu m AMD/ppm of ferrous iron (0.0007 gal H_2O_2/1000 gal AMD/ppm Fe^{2}).

Efficiencies in the ferric situation were grossly better (Table 16) than the ferrous situation. The 60-percent utilization efficiencies are in the same ballpark as the observations at Morton.[1] Virtually all aspects of effluent quality (Table 18) were better for the ferric situation.

Unfortunately, no explanation is readily available for the reason that limestone reacts better when the iron is in the ferric state. Discussion of this observation with a variety of investigators has shed no additional light on this situation.

Test Six - Sludge Recycling

To this point, the use of limestone in ferrous situations was not only grossly inefficient but was also incapable of producing a satisfactory effluent. Because three-fourths of the limestone was going directly to the sludge without reacting, sludge recycling was the logical step to increase utilization efficiency.

Process B utilized sludge recycling at a rate of approximately 16-percent of the AMD input rate of 1 liter/sec (16 gpm).

The results (Table 17) were encouraging, as Process B efficiency was 91 percent as opposed to the 17-percent value in Process A. Ferrous iron oxidation was better in Process B (93 vs 180 mg/l remaining in the effluent). Effluent suspended solids were equal for both processes.

Table 16. NEUTRALISATION DATA SUMMARIES FOR LIMESTONE @ 1 LITER/SEC WHERE HYDROGEN PEROXIDE WAS INJECTED INTO PROCESS B TO OXIDIZE THE FERROUS IRON

	Process	Mean	Std. Dev.
Effluent pH	A	6.42	0.09
	B	6.58	0.09
Neutraliser usage, kg/cu m	A	0.72	1.0
	B	1.06	0.2
Neutraliser usage, lbs/1000 gal	A	60.7	8.4
	B	8.8	1.6
Neutraliser usage, g/cu m/ppm influent acidity	A	4.50	1.8
	B	1.75	0.3
Cost, cents/1000 gal	A	10.48	4.6
	B	4.87	0.9
Cost, cents/cu m	A	3.30	1.2
	B	1.29	0.2
Cost, cents/10^3cu m/ppm influent acidity	A	3.46	0.2
	B	0.11	0.4
Utilisation efficiency, percent	A	19	3.0
	B	62	11
Stoichiometric factor (influent acidity)	A	4.3	1.8
	B	1.8	0.3
Sludge to waste, % of influent AMD	A	3.1	0.3
	B	0.6	0.3
Dry solids to waste, lbs/1000 gal	A	81.4	10.4
	B	11.0	4.0
Dry solids to waste, kg/cu m	A	9.86	1.3
	B	1.39	0.3
Underflow solids, percent	A	7.0	4.0
	B	4.0	1.0
Effluent turbidity, JTU	A	60	19
	B	48	5
Effluent suspended solids, mg/l	A	82	16
	B	35	3.6
Difference in reagent usage between Process A and B, percent		196	

Table 17. NEUTRALIZATION DATA SUMMARIES FOR LIMESTONE @ pH 6.5 AND 1 LITER/SEC WHERE PROCESS B EMPLOYED SLUDGE RECYCLE

	Process	Mean	Std. Dev.
Effluent pH	A	6.57	0.1
	B	6.50	0.1
Neutralizer usage, kg/cu m	A	2.53	0.3
	B	2.87	0.7
Neutralizer usage, lbs/1000 gal	A	20.3	2.6
	B	23.8	5.7
Neutralizer usage, g/cu m/ppm influent acidity	A	3.02	0.4
	B	3.41	0.1
Cost, cents/1000 gal	A	11.15	1.2
	B	13.08	3.4
Cost, cents/cu m	A	2.93	0.3
	B	3.08	0.1
Cost, cents/10^3cu m/ppm influent acidity	A	3.57	0.3
	B	3.71	0.1
Utilization efficiency, percent	A	17	3
	B	53	11
Stoichiometric factor (influent acidity)	A	5.0	0.6
	B	5.5	0.1
Sludge to waste, % of influent AMD	A	3.3	0.1
	A	3.7	0.1
Sludge recycled, % of influent AMD	A	0	0
	B	16.4	0.9
Dry solids recycled, lbs/1000 gal	A	0	0
	B	16.7	8.9
Dry solids to waste, lbs/1000 gal	A	10.8	0.6
	B	9.1	1.9
Dry solids to waste, kg/cu m	A	1.32	1.0
	B	0.98	0.9
Underflow solids, percent	A	9.1	0.3
	B	1.4	0.8
Effluent turbidity, JTU	A	97	11
	B	40	11
Reactor suspended solids, mg/l	A	1500	150
	B	2800	800
Effluent suspended solids, mg/l	A	97	66
	B	87	15
Difference in reagent usage between Process A and B, percent		180	

Automatic pH control was not used for this study. The speeds of both dry feeders were adjusted manually. Control-probe fouling was more severe in recycling situations and was particularly bad in the pH range below 7.5.

Sludge solids were reduced from 5 to 1.4 percent by recycling because the increased utilization efficiency reduced the quantity of unreacted limestone.

Although efficiency was improved by recycling, effluent quality remained undesirable.

Test Seven - Recycle Rate

As the previous test had shown the efficacy of sludge recycling, it was necessary to determine the rate of recycling that was most effective. The hydraulic limitations of the equipment restricted flows to less than 1.1 liter/sec (18 gpm). It was not possible, therefore, to increase the recycling rate beyond the 16-percent rate of Test Six. To circumvent the hydraulic limitations and increase the proportion of sludge recycled, the influent flow rates on both processes were lowered to 0.5 liter/sec (8 gpm). The recycling rate of Process A was adjusted to 16 percent (to be the same as Test Six) and Process B recycled 61 percent. Actual flow rates through both processes were:

Process A - 0.5 liter/sec AMD + 0.1 liter/sec sludge recycle = 0.6 liter/sec (8 gpm AMD + 1.6 gpm sludge recycle = 9.6 gpm)

Process B - 0.5 liter/sec AMD + 0.3 liter/sec sludge recycle = 0.8 liter/sec (8 gpm AMD + 4.8 gpm sludge recycle = 12.8 gpm)

There is significant time lag at 0.5 liter/sec between the inputs and outlets of the system. This makes the reactions difficult to control automatically (manual pH control was used) and also requires a long time to establish equilibrium conditions. Since each entire system holds 44 cu m (11,600 gal), a once-thru detention time is 24 hr at a 0.5-liter/sec (8-gpm) flow rate.

The results of the study (Tables 18 and 19) were felt to be questionable because of the variation and trends of the data throughout the duration (6 days) of the study. Efficiencies in both processes began near 200 percent and generally decreased during the course of the test. It was impractical to invest additional time in this particular investigation. The significant findings from this study were:

Table 18. NEUTRALIZATION DATA SUMMARIES FOR LIMESTONE @ pH 6.5 AND 0.5 LITER/SEC WHERE PROCESS A UTILIZED A 10-PERCENT RECYCLE RATE AND PROCESS B UTILIZED A 60-PERCENT RATE

	Process	Mean	Std. Dev.
Effluent pH	A	6.57	0.1
	B	6.55	0.1
Neutralizer usage, kg/cu m	A	0.75	0.1
	B	0.50	0.2
Neutralizer usage, lbs/1000 gal	A	6.2	0.7
	B	4.1	1.8
Neutralizer usage, g/cu m/ppm influent acidity	A	1.09	0.3
	B	0.73	0.4
Cost, cents/1000 gal	A	3.07	0.8
	B	2.11	1.2
Cost, cents/cu m	A	0.81	0.2
	B	0.56	0.1
Cost, cents/10^3cu m/ppm influent acidity	A	1.19	0.4
	B	0.80	0.4
Utilization efficiency, percent	A	93	15
	B	101	66
Stoichiometric factor (influent acidity)	A	1.09	0.3
	B	0.73	0.4
Sludge to waste, % of influent AMD	A	2.7	0.2
	B	6.5	3.0
Sludge recycled, % of influent AMD	A	15.7	0.8
	B	60.6	4.9
Dry solids recycled, lbs/1000 gal	A	53	52
	B	54	19
Dry solids to waste, lbs/1000 gal	A	2.0	0.0
	B	4.3	2.7
Dry solids to waste, kg/cu m	A	1.08	1.1
	B	0.59	0.3
Underflow solids, percent	A	3.2	1.2
	B	0.8	0.3
Effluent turbidity, JTU	A	85	8
	B	50	19
Reactor suspended solids, mg/l	A	500	1600
	B	480	870
Effluent suspended solids, mg/l	A	89	88
	B	47	35
Difference in reagent usage between Process A and B, percent		50	

1. The effluent quality of Process A was significantly better than Process B.
2. The ferrous iron in effluent A was consistently and significantly lower than B because the pH of A was slightly higher and the effective detention time in the B aerator was less. As both processes were recycling sludge (predominantly ferric hydroxide), they weren't recycling ferrous iron, per se. Since the throughput rate in the F aerator was 0.8 liter/sec (18.8 gpm) as contrasted with 0.6 liter/sec (9.2 gpm) in Process B, the effective oxidation contact time in Aerator B was 30 percent less than Process A. Any gains in utilisation efficiency were more than offset by losses in oxidation capability.

Even at 0.9 liter/sec, the effluent ferrous iron values in Process B were still near 80 mg/l.

Test Eight - Two Aerators In Series

At this point in time, it was apparent that although the limestone process could probably be cost-competitive with lime, serious shortcomings still existed in effluent quality (specifically iron oxidation).

To further investigate the iron oxidation problems, the aerators from both Process A and B were connected in series to double the oxidation capability. A larger mixer (Lightnin' Model MD-48) was installed on the limestone reactor. A study was conducted utilising this two-aerator mode with a 0.63-liter/sec (10-gpm) flow rate, manual pH control, and an 18-percent recycling rate. Results of this study (Tables 19 and 18) indicated that sludge recycling could increase the effluent pH to near 7 and could sustain the pH at that point. All ferrous iron was oxidised, utilisation efficiencies were near 80 percent, and effluent quality was significantly improved over earlier studies. The effluent total iron was high (23 mg/l), but practically all of it was suspended iron, as filtered samples contained only 1.8 mg/l of dissolved iron. It was felt that the addition of coagulant aids would improve the effluent quality sufficiently to enable compliance with existing effluent standards. At the 0.63-liter/sec flow rate, the detention time in the aeration system (both aerators) was 6 hr.

Table 19. NEUTRALIZATION DATA SUMMARIES FOR LIMESTONE @ pH 7 AND 0.65 LITER/SEC UTILIZING TWO AERATORS IN SERIES

	Mean	Std. Dev.
Effluent pH	7.19	0.1
Neutralizer usage, kg/cu m	0.93	0.04
Neutralizer usage, lbs/1000 gal	7.7	0.3
Neutralizer usage, g/cu m/ppm influent acidity	1.06	0.1
Cost, cents/1000 gal	4.09	0.2
Cost, cents/cu m	1.12	0.1
Cost, cents/10^3cu m/ppm influent acidity	1.53	0.1
Utilization efficiency, percent	83	6.9
Stoichiometric factor (influent acidity)	1.06	0.1
Sludge to waste, % of influent AMD	1.9	0.1
Sludge recycled, % of influent AMD	18.0	0.9
Dry solids recycled, lbs/1000 gal	42	11
Dry solids to waste, lbs/1000 gal	4.9	1.2
Dry solids to waste, kg/cu m	0.54	0.1
Underflow solids, percent	0.6	0.6
Effluent turbidity, JTU	97	11
Reactor suspended solids, mg/l	7150	450
Effluent suspended solids, mg/l	31	0

Test Nine - Two Aerators in Series @ 0.9 Liter/Sec

Because the results of Test Eight were encouraging, the flow rate through the system was increased from 0.63 liter/sec to 0.9 liter/sec to determine if sufficient oxidation could be maintained with the shorter detention time. Manual pH control was again utilized and sludge was recycled at an 18-percent (of the influent AMD) rate.

Effluent pH's (Table 20) were sustainable near 7. Utilization efficiency averaged 50 percent. Effluent ferrous iron averaged 2.4 mg/l, indicating incomplete oxidation at the higher flow rate. Total iron (table 19) in the effluent was 29 mg/l, and the filtered samples contained 6.7 mg/l. Total system performance at this flow rate was inferior to that of Test Eight. Oxidation detention time during this test was 4 hr at the 0.9-liter/sec flow rate.

Test Ten - Two Aerators in Series @ 0.63 Liter/Sec With Coagulant Addition

The use of coagulants was studied on limestone treatment to attempt to improve effluent clarity and quality. Dowell M144 was injected at a 7-mg/l rate into the 2.5-cm (1-in) line from the aerator discharge pump to the thickener influent. The limestone feed rate was manually controlled. Both aerators were connected in series, and the water flow rate was 0.63 liter/sec (10 gpm). The results indicated that coagulant addition (Table 21 and 19) was very successful in improving effluent quality. Effluent turbidity was reduced from 97 JTU (Table 19 - earlier test without coagulants) to 19 JTU; effluent iron was reduced from 23 mg/l to 1.8; and suspended solids were lowered from 31 mg/l to 9. Total chemical costs for this treatment were 1.3 cents/cu m (5 cents/1000 gal) for limestone plus 2.6 cents/cu m (10 cents/1000 gal) for coagulant. As the coagulant addition was not optimized, some improvement could be made in this figure.

Test Eleven - Two Aerators in Series @ 0.9 Liter/Sec With Coagulant Addition

The AMD flow rate was increased in this test to 0.9 liter/sec (14 gpm) while maintaining approximately a 7-mg/l injection rate of M144 coagulant. Effluent turbidity was not adversely affected by the increased flow rate (Table 22) but effluent iron values were somewhat higher than the previous test (3.4 vs 0.9 mg/l - Table 19) at the lower flow rate.

Table 50. NEUTRALISATION DATA SUMMARIES FOR LIMESTONE @ pH 7 AND 0.9 LITER/SEC UTILIZING TWO AERATORS IN SERIES

	Mean	Std. Dev.
Effluent pH	6.94	0.3
Neutraliser usage, kg/cu m	1.24	0.1
Neutraliser usage, lbs/1000 gal	10.4	0.4
Neutraliser usage, g/cu m/ppm influent acidity	2.17	0.3
Cost, cents/1000 gal	9.70	0.8
Cost, cents/cu m	1.91	0.1
Cost, cents/10^3cu m/ppm influent acidity	2.63	0.4
Utilisation efficiency, percent	91	9.9
Stoichiometric factor (influent acidity)	2.09	0.4
Sludge to waste, % of influent AMD	2.2	0.1
Sludge recycled, % of influent AMD	17.9	0.7
Dry solids recycled, lbs/1000 gal	90	28
Dry solids to waste, lbs/1000 gal	6.1	3.5
Dry solids to waste, kg/cu m	0.73	0.4
Underflow solids, percent	3.3	1.9
Effluent turbidity, JTU	84	9
Reactor suspended solids, mg/l	4470	930
Effluent suspended solids, mg/l	43	7

Table 21. NEUTRALIZATION DATA SUMMARIES FOR LIMESTONE USING TWO AERATORS IN SERIES @ 0.63 LITER/SEC (10 GPM) WITH COAGULANT ADDITION

	Mean	Std. Dev.
Effluent pH	7.3	0.2
Neutraliser usage, kg/cu m	1.06	0.3
Neutraliser usage, lbs/1000 gal	8.9	2.8
Neutraliser usage, g/cu m/ppm influent acidity	0.38	0.7
Cost, cents/1000 gal	4.00	1.2
Cost, cents/cu m	1.09	0.3
Cost, cents/10^3cu m/ppm influent acidity	0.39	0.9
Utilisation efficiency, percent	48	14
Stoichiometric factor (influent acidity)	2.24	0.9
Sludge to waste, % of influent AMD	2.0	0.2
Sludge recycled, % of influent AMD	86	3
Dry solids recycled, lbs/1000 gal	46	24
Dry solids to waste, lbs/1000 gal	3.8	1.7
Dry solids to waste, kg/cu m	0.46	0.2
Underflow solids, percent	2.3	1.0
Effluent turbidity, JTU	12	6
Reactor suspended solids, mg/l	5600	3300
Effluent suspended solids, mg/l	8.8	4.0

Table 22. NEUTRALIZATION DATA SUMMARIES FOR LIMESTONE USING TWO AERATORS IN SERIES @ 0.9 LITER/SEC (14 GPM) WITH COAGULANT ADDITION

	Mean	Std. Dev.
Effluent pH	7.3	0.1
Neutraliser usage, kg/cu m	.77	0.8
Neutraliser usage, lbs/1000 gal	6.40	1.6
Neutraliser usage, g/cu m/ppm influent acidity	1.58	0.4
Cost, cents/1000 gal	3.58	0.9
Cost, cents/cu m	0.93	0.2
Cost, cents/10^3cu m/ppm influent acidity	1.85	0.5
Utilization efficiency, percent	66	11
Stoichiometric factor (influent acidity)	1.64	0.3
Sludge to waste, % of influent AMD	1.5	0.1
Sludge recycled, % of influent AMD	18.6	0.8
Dry solids recycled, lbs/1000 gal	28	21
Dry solids to waste, lbs/1000 gal	2.8	1.2
Dry solids to waste, kg/cu m	0.34	0.1
Underflow solids, percent	2.3	1.0
Effluent turbidity, JTU	8.1	3.7
Reactor suspended solids, mg/l	10200	4700
Effluent suspended solids, mg/l	9.3	4.1

Discussion of Limestone Studies

Several advantages and disadvantages to the use of limestone were noted during the course of these investigations. Chief among the advantages was the reagent usage cost that was, for the optimum case (Test Eight), on the order of 1.3 cents/cu m (5 cents/1000 gal). Sludge solids content during many of the tests was near 10 percent by weight. This solids advantage may be more apparent than real, however, since much of the weight content is unreacted limestone. The presence of unreacted limestone in the sludge is obviously undesirable. Sludge recycling is a necessity because such a large quantity of limestone ends up in the sludge.

On the disadvantage side, many comments can be made on the application of limestone to ferrous iron situations. The low effluent pH (below 7.5) requires excessive detention time in the oxidation system to enable adequate ferrous to ferric conversion. This detention time requirement at Crown was on the order of five to six hr. These long reaction and oxidation times would require excessive energy input per unit volume of water for mixing and oxidation processes and would similarly require large capital expenditures and facility space for equipment.

The effluent turbidity for limestone-treated waters is high. Charles Ford[8] of Bituminous Coal Research noted the high turbidity and felt that it was caused by colloidal particles of limestone that remain in suspension. Filtered effluent samples are quite clear and free from turbidity and color. Coagulants are very effective in improving the turbidity problem associated with the use of limestone, but their cost often exceeds the cost for the limestone.

Operational difficulties associated with limestone treatment centered around the accumulation of solids in the bottom of the aeration tanks where violent mixing was not present. The solids and inerts in the sludge also caused failure of the automatic valving by scoring the ball valves. This erosion problem was overcome by using different valves, but it illustrated the potential of the limestone for wear on moving parts. Because of the high density of the limestone sludge, it was difficult to handle and move. It demonstrated a tendency to bridge and rathole in the thickener. Periodic cleaning the accumulation from the bottom of the aerators was a major task.

The low effluent pH of limestone-neutralised AMD was in the range (below pH 7.5) where maximum probe fouling problems occurred. Automatic pH control in this situation was ineffective because of rapid fouling. Use of coagulants, however, reduced the severity of the pH probe fouling problem.

In summary, although the limestone process was demonstrated to be technically applicable for use on the majority of ferrous waters, it was felt that the process simply wasn't feasible because of the aforementioned reasons. In contrast, as demonstrated in Test Five, the limestone reagent works quite well on ferric iron situations.

FULL-SCALE, CONTINUOUS-FLOW STUDIES ON HYDRATED-LIME NEUTRALISATION

Introduction

Background data for lime--$Ca(OH)_2$--neutralisation is readily available from a variety of sources. Approximately 300 AMD treatment plants using lime are currently in operation in the Appalachian mining states alone. Although a wealth of data was available on the subject, it was necessary to develop background data on Crown AMD and EPA equipment to enable comparisons with other treatment techniques at the Crown Field Site.

The EPA equipment provided 7.3 min of detention time in the lime reactor at 1 liter/sec (16 gpm). Approximately 2 hr of detention time was provided in the aerator and 10 hr of settling time was available in the thickener.

Cost figures for lime requirements are based upon $38.58/tonne ($35.00/ton) in bulk.

The investigations on hydrated-lime treatment basically followed the research plan outlined in Table 23.

Effect of pH

Tests to investigate the operational and effluent quality and to generate basic data were conducted by varying the pH from 5.5 to 10. Tables 24 and 25 illustrate typical data from the neutralisation tests. Optimum results in terms of effluent quality were obtained between pH 8 and 8.5. Lime utilisation efficiency in this range was better than 60 percent. No significant change in total dissolved solids (TDS) was observed throughout the pH range of the study. Effluent iron values around 4 mg/l (@ pH 8 to 8.5) were predominately caused by suspended ferric hydroxide as filtered samples indicated less than 0.5 mg/l of iron. It was felt that the use of

Table 23. RESEARCH PLAN FOR LIME NEUTRALIZATION

Order of study	Variable	Action investigated
1	pH	Effect on effluent quality
2	Sludge recycling	Effect on quality and sludge
3	Rate of recycling	Effect on sludge density
4	Coagulant addition	Effect on effluent quality
5	Ferrous hydroxide precipitation	Effect on effluent quality
6	Sludge density	Effect on sludge density

| | | |

Table 25. [illegible]

[illegible]	Raw water	[illegible] at specified pH									
pH	4.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
Acidity	730	480	120	25	5	0	0	0	0	0	0
Calcium	350	380	440	530	570	590	630	660	630	620	640
Magnesium	120	140	120	110	100	120	100	70	50	37	25
Total iron	330	260	62	11	8.5	6.0	5.0	3.0	3.0	2.6	1.0
Total iron, filtered sample	330	250	50	5	0.2	0.3	0.2	0.4	0.3	0.5	0.5
Ferrous iron	330	250	46	6.3	2.0	0	0	0	0	0	0
Sulfate	550	560	560	550	550	550	550	540	530	480	470
Alkalinity	25	3.5	2.1	1.5	1.4	1.4	0.9	1.0	0.9	1.0	0.8
Alkalinity, filtered sample	21	3.0	1.7	0.9	1.0	0.6	0.6	0.8	0.3	0.5	0.3
Manganese	6	5.7	4.5	4	3	4	3	0.5	0.2	0.2	0.1
Solids	3200	3100	2900	3400	3300	3300	3300	2900	2900	3000	2900
Acidity	0	4.6	12	22	53	60	110	80	55	42	34
Total dissolved solids	440	430	400	420	420	400	400	430	400	430	400

[illegible] All values are mg/l, except for pH. All values are mean. Acidity and alkalinity are expressed as $CaCO_3$.

coagulants would improve the effluent iron and turbidity levels. This was confirmed in later studies.

Stoichiometric lime requirements ranged from 1.2 to 1.7 times the amount of acidity (as determined by titration to pH 7.3) to treat the AMD between pH 8 to 8.5. The cost for lime usage was increased by 40 percent by increasing the effluent pH from 8 to 8.5. Treatment to pH 8.5 was 70 percent more expensive in terms of lime usage than treatment to pH 7.0.

Treatment above pH 8.5 did not increase effluent alkalinity. The strong relationship between lime-usage cost and treatment pH is shown in Figure 17. A definite inflection point was observed on the curve between pH 7.5 and 8.5.

Sludge volumes collected in 1000-ml graduates increased virtually linearly with pH, as shown in Figure 18. An overlay of effluent turbidity is also shown in this figure.

All the initial background studies were made using a sludge pumping rate to waste of 6-percent of the influent AMD rate. A plot of underflow solids levels and the dry solids production at the 6-percent sludge pumping rate are contrasted with the same parameters at a 2.8-percent pumping rate in Figure 19.

Effect of Sludge Recycling

A sludge recycling rate of 20 percent of the influent AMD flow was studied in Process B as compared to no recycling in Process A. This study was made using AMD flows of 0.95 liter/sec (15 gpm) treated to pH 8.0.

Results (Tables 26 and 27) indicated that a slight increase in lime utilization efficiency was obtained by recycling (81 vs 74 percent). Although the reactor suspended solids were much higher on B (because of the sludge recycling), the effluent suspended solids levels were similar (35 vs 28 mg/l) as were the effluent turbidity values (29 vs 25 JTU). Effluent iron values (Table 27) were lower in B than in A (12 vs 5.1 mg/l), apparently because the higher influent solids level in the recycling process was more effective in settling the suspended iron. Filtered samples of the effluents from both processes contained less than 1 mg/l total iron.

The apparent increase in efficiency observed in Process B was probably caused by the bulk lime absorbing carbon dioxide and partially recarbonating, thus reducing the reactivity per unit volume. Recycling increased the

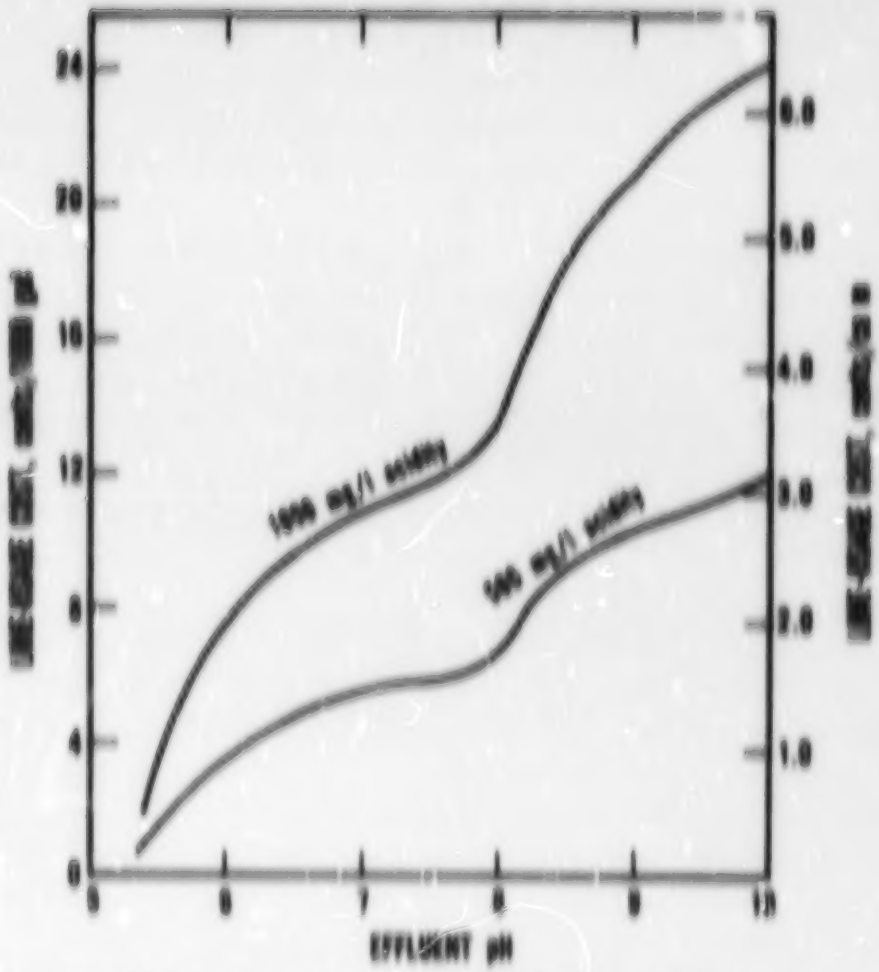


Figure 17. Effect of the treatment pH on lime usage costs.

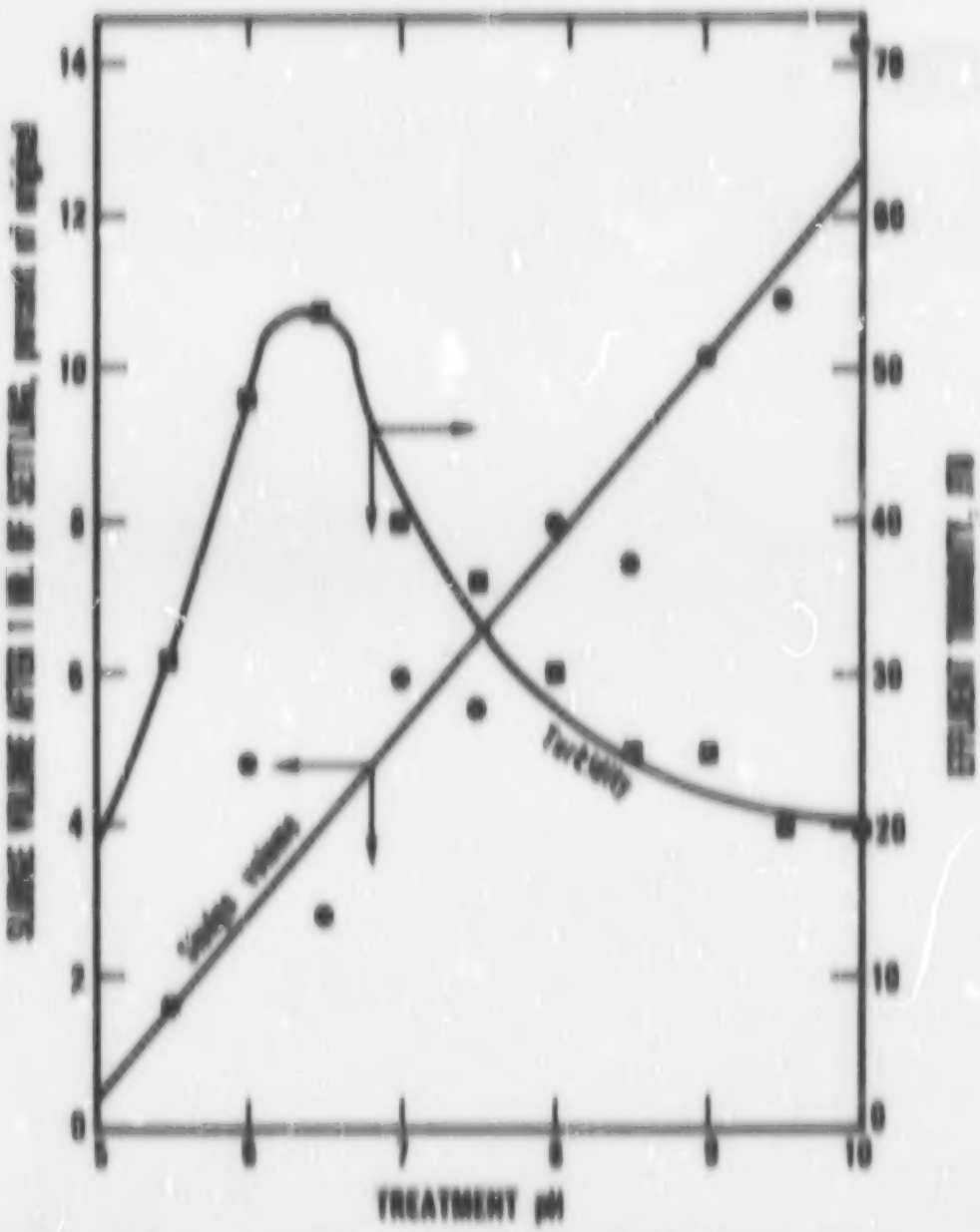


Figure 18. Sludge volume and effluent turbidity after 1-hour settling time as functions of treatment pH for the lime neutralization tests.

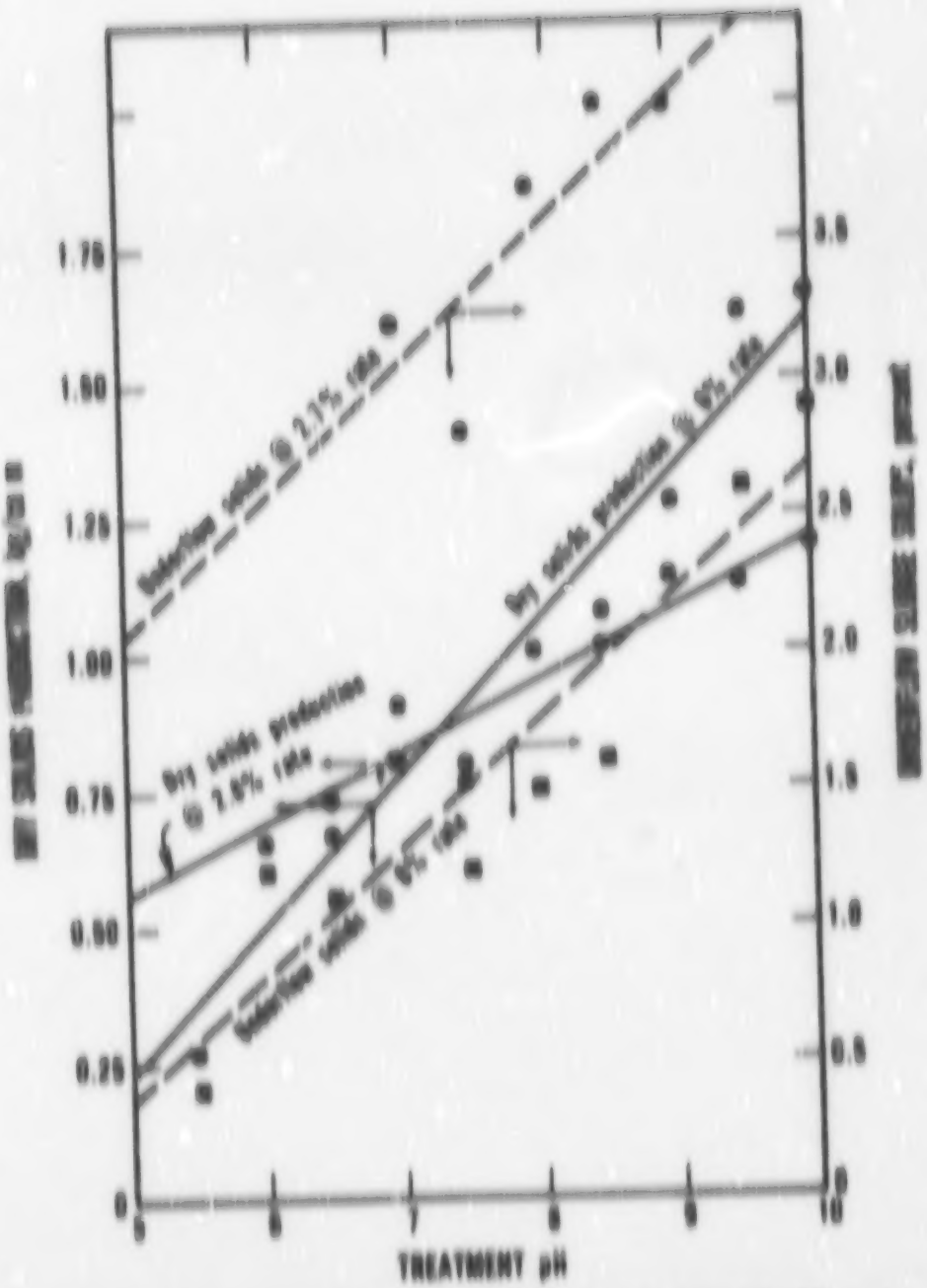


Figure 18. Underflow solids concentration at approximately 6% and 2.5% pumping rates and the dry solids production rate for the lime neutralization tests.

Table 26. NEUTRALISATION DATA SUMMARIES FOR LIME NEUTRALISATION @ pH 8.0 AND 0.99 LITER/SEC UTILIZING SLUDGE RECYCLE (20 PERCENT RATE) ON PROCESS B

	Process	Mean	Std. Dev.
Effluent pH	A	8.00	0.09
	B	8.01	0.06
Neutralizer usage, kg/cu m	A	0.64	0.07
	B	.58	0.06
Neutralizer usage, lbs/1000 gal	A	5.32	0.6
	B	4.85	0.7
Neutralizer usage, g/cu m/ppm influent acidity	A	1.18	0.1
	B	1.08	0.1
Cost, cents/1000 gal	A	2.33	1.1
	B	0.49	1.0
Cost, cents/cu m	A	0.16	0.3
	B	0.01	0.3
Cost, cents/10^3cu m/ppm influent acidity	A	4.35	0.6
	B	4.16	0.5
Utilization efficiency, percent	A	75	0.9
	B	81	0.1
Stoichiometric factor (influent acidity)	A	1.32	0.2
	B	1.54	0.2
Sludge to waste, % of influent AMD	A	2.2	0.2
	B	2.7	0.1
Sludge recycled, % of influent AMD	A	0	0
	B	19.4	1.1
Dry solids recycled, lbs/1000 gal	A	0	0
	B	51	6
Dry solids to waste, lbs/1000 gal	A	6.8	0.6
	B	7.1	1.2
Dry solids to waste, kg/cu m	A	0.81	0.1
	B	0.85	0.1
Underflow solids, percent	A	0.8	0.2
	B	1.1	0.8
Effluent turbidity, JTU	A	85	3.1
	B	89	14
Reactor suspended solids, mg/l	A	250	850
	B	5100	1375
Effluent suspended solids, mg/l	A	15	17
	B	84	88
Difference in reagent usage between Process A and B, percent		9.5	

| | | |

[illegible]

[illegible]

[illegible]

| | | |

effective reaction/mixing time of the calcium carbonate portion of the neutralising agent and allowed greater utilisation. Tests of the purity of the bulk lime itself indicated a CaO equivalence of 66 percent as compared to the minimum composition of 78 percent for fresh lime (Table 3).

Effect of Sludge Recycle Rate

In the interim between this and the previous series of tests, several changes were made in the facility during a 2-month downtime caused by pump failure. New bottom mixers were installed on the aerator turbines in an attempt to eliminate solids accumulation in the aeration tanks. A new load of hydrated lime was obtained. Analyses of the lime indicated a $Ca(OH)_2$ equivalence of 93 percent, a $CaCO_3$ equivalence of 125 percent, and a CaO equivalence of 73 percent.

For this and future specialised studies, an additional pump was installed on each aerator to increase the flow capability from 1.25 to 2.5 liters/sec (20 to 40 gpm). This study compared a 10-percent (of the influent AMD) recycling rate (Process A) to a 30-percent (Process B) rate. Both processes treated 1 liter/sec (16 gpm) to pH 8.0. Results of the study indicated that no increase in efficiency or improvement in effluent quality was obtained from a higher recycling rate (Tables 27 and 28).

Effect of Coagulants on Effluent Quality

Several Dewell coagulants were tested in bench-scale studies to provide guidance to plant studies. The anionic coagulants as a group were much more effective than either non-ionic or cationic forms. In the EPA application, Dewell M144 appeared to be most effective. Although lab studies indicated that a 1-mg/l addition rate was adequate, a 2-mg/l rate was necessary for successful plant operation. The M144 was injected into the 2.5-cm (1-in) line leading from the discharge of the single aerator pump to the thickener inlet.

Two studies were made on coagulant usage. The first study compared coagulant vs no-coagulant at pH 8; the second compared coagulant at pH 8 vs coagulant at pH 7.

Coagulant vs No-Coagulant at pH 8--

The M144 at 2 mg/l was quite effective in improving clarification as shown in Tables 29 and 27. Effluent turbidity was significantly better on the coagulant process (A) as compared to no coagulant (B), i.e., 7 vs 85 JTU.

Table 28. NEUTRALIZATION DATA SUMMARIES FOR LIME @ 1 LITER/SEC WHERE PROCESS A UTILIZED A 10-PERCENT SLUDGE RECYCLE RATE AND PROCESS B UTILIZED A 30-PERCENT RATE

	Process	Mean	Std. Dev.
Effluent pH	A	7.9	0.1
	B	7.9	0.2
Neutraliser usage, kg/cu m	A	0.67	0.03
	B	0.70	0.05
Neutraliser usage, lbs/1000 gal	A	5.58	0.3
	B	5.84	0.4
Neutraliser usage, g/cu m/ppm influent acidity	A	1.40	0.0
	B	1.46	0.2
Cost, cents/1000 gal	A	9.8	0.4
	B	10.2	0.6
Cost, cents/cu m	A	0.36	0.1
	B	0.70	0.2
Cost, cents/10^3cu m/ppm influent acidity	A	5.39	0.8
	B	5.61	0.6
Utilization efficiency, percent	A	68	7.2
	B	61	7.8
Stoichiometric factor (influent acidity)	A	1.89	0.1
	B	1.97	0.3
Sludge to waste, % of influent AMD	A	1.06	0.02
	B	1.20	0.05
Sludge recycled, % of influent AMD	A	10.1	0.3
	B	29.0	0.7
Dry solids recycled, lbs/1000 gal	A	80	10
	B	150	21
Dry solids to waste, lbs/1000 gal	A	7.5	0.4
	B	8.2	1.0
Dry solids to waste, kg/cu m	A	0.93	0.3
	B	0.74	0.1
Underflow solids, percent	A	7.3	0.1
	B	8.1	0.9
Effluent turbidity, JTU	A	30	10
	B	24	21
Reactor suspended solids, mg/l	A	7000	550
	B	15300	9300
Effluent suspended solids, mg/l	A	37	17
	B	51	14
Difference in reagent usage between Processes A and B, percent		4.6	

Table 29. NEUTRALISATION DATA SUMMARIES FOR LIME @ 0.5 LITER/SEC (10 GPM) AND pH 8 WHERE PROCESS A UTILIZED COAGULANT ADDITION

	Process	Mean	Std. Dev.
Effluent pH	A	8.0	0.05
	B	8.0	0.06
Neutralizer usage, kg/cu m	A	0.76	0.1
	B	0.75	0.1
Neutralizer usage, lbs/1000 gal	A	6.4	0.8
	B	6.2	0.8
Neutralizer usage, g/cu m/ppm influent acidity	A	1.36	0.2
	B	1.50	0.2
Cost, cents/1000 gal	A	11.2	1.8
	B	10.8	0.9
Cost, cents/cu m	A	2.95	0.5
	B	2.85	0.2
Cost, cents/10^3cu m/ppm influent acidity	A	6.00	0.9
	B	5.77	0.6
Utilization efficiency, percent	A	57	10
	B	58	6.9
Stoichiometric factor (influent acidity)	A	2.09	0.3
	B	2.04	0.2
Sludge to waste, percent of influent AMD	A	0.5	0.05
	B	0.5	0.08
Sludge recycled, percent of influent AMD	A	99.7	0.5
	B	99.5	0.5
Dry solids recycled, lbs/1000 gal	A	48	16
	B	60	26
Dry solids to waste, lbs/1000 gal	A	4.3	1.5
	B	7.5	2.5
Dry solids to waste, kg/cu m	A	0.50	0.2
	B	0.89	0.3
Underflow solids, percent	A	0.13	0.7
	B	3.60	1.2
Effluent turbidity, JTU	A	7	1.5
	B	25	6.2
Reactor suspended solids, mg/l	A	5000	2000
	B	8600	2700
Effluent suspended solids, mg/l	A	8.0	5.7
	B	18	10
Difference in reagent usage between Process A and B, percent		5.4	

effluent iron values were similarly improved (1.4 vs 3.3 mg/l). These tests were conducted at AMD flow rates of 0.6 liter/sec (10 gpm) and recycling raves of 23 percent of the influent AMD.

The Dowell M144 cost approximately $3.64/kg ($1.65/lb) in bulk. The add-on cost of a 2-mg/l addition rate amounts to 0.7 cents/cu m (2.7 cents/1000 gal).

Coagulant at pH 8 vs Coagulant at pH 7--

All flow rates were the same as the previous test. M144 was injected into both processes at rates between 2 and 3 mg/l. The effluent pH on Process B was lowered to pH 7; Process A was maintained at pH 8. Effluent quality at pH 7 could not match the pH 8 conditions (Tables 27 and 30) in terms of turbidity (27 vs 7 JTU), suspended solids (13 vs 9 mg/l), and iron (10 vs 2.1 mg/l). During this particular comparison, twice as much lime was required to treat to pH 8 than to pH 7.

Effluent quality at pH 7 was enhanced by the use of coagulants as compared to earlier studies (Tables 24 and 25); e.g., suspended solids were lower (13 vs 33 mg/l), iron was comparable (10 vs 8.5 mg/l), and turbidity was improved (27 vs 40 JTU).

Coagulant at pH 8 With Sludge Recycle vs Coagulant at pH 8 and No Recycle--

Coagulants were injected into both processes at a 3-mg/l rate. Flows were maintained at 0.9 liter/sec (14 gpm) for each process. Process A recycled no sludge; Process B recycled sludge at a 16-percent rate. In Table 31, the efficacy of sludge recycling is again demonstrated by the higher utilization efficiencies observed in Process B as compared to A (79 vs 61 percent). Very little difference was noted in effluent quality from the processes.

Effect of Ferrous Hydroxide Precipitation

Current treatment techniques in Europe[9] emphasize the possibility of eliminating the oxidation step from the neutralization process and precipitating the iron as ferrous hydroxide at pH's around 9. Although the ferrous hydroxide will, in most cases, eventually oxidize to ferric and release additional acidity, sufficient buffering capacity is available at the higher pH to compensate for the additional H^+ ions.

Three studies were made on this concept at the Crown facility. In the first, the AMD was mixed with lime and pumped directly to the thickener.

Table 10. NEUTRALIZATION DATA SUMMARIES FOR LIME @ 0.6 LITER/SEC (10 GPM) USING COAGULANT AND COMPARING pH 6 (PROCESS A) VS pH 7 (PROCESS B)

	Process	Mean	Std. Dev.
Effluent pH	A	7.01	0.1
	B	6.91	0.1
Neutralizer usage, kg/cu m	A	0.730	0.1
	B	0.462	0.1
Neutralizer usage, lbs/1000 gal	A	6.0	0.8
	B	3.8	0.9
Neutralizer usage, g/cu m/ppm influent acidity	A	1.51	0.2
	B	0.74	0.1
Cost, cents/1000 gal	A	10.8	1.0
	B	5.3	0.8
Cost, cents/cu m	A	2.85	0.3
	B	1.40	0.2
Cost, cents/10^3cu m/ppm influent acidity	A	5.84	0.7
	B	2.83	0.2
Utilization efficiency, percent	A	53	7
	B	100	0
Stoichiometric factor (influent acidity)	A	2.03	0.2
	B	0.99	0.1
Sludge to waste, % of influent AMD	A	3.6	0.2
	B	3.5	0.3
Sludge recycled, % of influent AMD	A	29.5	0.7
	B	96.5	0.5
Dry solids recycled, lbs/1000 gal	A	86	48
	B	93	58
Dry solids to waste, lbs/1000 gal	A	7.6	1.2
	B	8.9	1.4
Dry solids to waste, kg/cu m	A	0.90	0.2
	B	1.08	0.2
Underflow solids, percent	A	3.2	0.1
	B	4.3	1.6
Effluent turbidity, FTU	A	7	0.3
	B	87	11
Reactor suspended solids, mg/l	A	8000	1500
	B	8800	980
Effluent suspended solids, mg/l	A	0.3	0.5
	B	13.3	8.1
Difference in reagent usage between Process A and B, percent		104	

Table 11. NEUTRALISATION DATA SUMMARIES FOR LIME @ 0.9 LITER/SEC AND pH 8 USING COAGULANTS WHERE PROCESS B UTILISED SLUDGE RECYCLE

	Process	Mean	Std. Dev.
Effluent pH	A	7.0	0.0
	B	7.0	0.1
Limestone usage, kg/cu m	A	0	0
	B	0	0
Lime usage, kg/cu m	A	0.68	0.01
	B	0.54	0.01
Cost, cents/1000 gal	A	9.93	1.1
	B	7.91	1.0
Cost, cents/cu m	A	0.61	0.1
	B	0.49	0.1
Cost, cents/10^3cu m/ppm influent acidity	A	1.40	0.5
	B	1.04	0.5
Utilization efficiency, percent	A	61	3.5
	B	79	7.6
Stoichiometric factor (influent acidity)	A	1.00	0.0
	B	1.50	0.0
Sludge to waste, % of influent ABD	A	0.5	0.0
	B	0.0	0.0
Sludge recycled, % of influent ABD	A	0	-
	B	15.0	0.7
Dry solids recycled, lbs/1000 gal	A	0	-
	B	45	00
Dry solids to waste, lbs/1000 gal	A	5.1	0.7
	B	6.0	1.0
Dry solids to waste, kg/cu m	A	0.61	0.1
	B	0.71	0.1
Underflow solids, percent	A	0.8	0.5
	B	1.5	1.7
Effluent turbidity, JTU	A	10	5.0
	B	7.2	0.9
Limestone reactor suspended solids, mg/l	A	-	-
	B	-	-
Lime reactor suspended solids, mg/l	A	800	650
	B	8300	1700
Effluent suspended solids, mg/l	A	3.2	0.0
	B	8.8	3.7
Difference in reagent usage cost between Process A and B, percent		28	

The mixer on the lime reactor was replaced with a small bench-scale mixer to provide minimal agitation and minimal opportunity for oxidation to occur in the reactor. A 1-liter/sec flow (16 gpm) was treated to pH 9. No sludge recycle or coagulant was added. The results of the test (Table 32 and 27) indicated unexplained high-lime requirements as compared to earlier tests using aeration at pH 9. Utilization efficiency averaged near 44 percent, and the stoichiometric factor was 2.7 as compared to earlier ferric values of 56 and 1.9, respectively. The effluent quality of the ferrous process was comparable to earlier ferric conditions (e.g., turbidities were 26 vs 25 JTU, suspended solids were 23 vs 35 mg/l, and effluent iron levels were 4 vs 3 mg/l).

The ferrous hydroxide sludge exhibited very large floc size and slow compaction characteristics. In comparison with ferric sludges, the ferrous sludges occupied more than 1.5 times the volume.

In the second study of this series, Nalco coagulant was injected at approximately a 5-mg/l rate while maintaining the same basic operating parameters as in the first study.

The coagulant addition greatly improved settling rates of the ferrous sludge but did little for effluent clarity or quality (Tables 33 and 27).

Because of the unexplained high-lime requirement observed in the first ferrous hydroxide study, an additional test was made directly comparing ferrous (Process A) vs ferric hydroxide (Process B) conditions while keeping all other parameters the same. The results (Tables 34 and 27) indicated virtually identical lime requirements for both processes. Both processes utilized coagulant addition rates near 5 ppm. Effluent quality characteristics of the ferric hydroxide situation were significantly superior to the ferrous; e.g., turbidity was 5 vs 20 JTU, suspended solids averaged 6.0 vs 29 mg/l, and total iron values were 1.7 vs 6.7 mg/l.

The continuing low utilization efficiencies of the lime remain unexplained.

Sludge Density Study

A limited attempt was made to maximize the sludge density obtainable under the conditions at the Crown Field Site. For this purpose, a test was conducted using lime neutralization to pH 9 and operating at a 1-liter/sec (16-gpm) AMD flow rate. Sludge was continuously recycled into the reactor

Table 12. NEUTRALISATION DATA SUMMARISED FOR LIME @ 1 LITRE/SEC AND pH 9 USING NO AERATION (FERROUS HYDROXIDE PRECIPITATION)

	Mean	Std. Dev.
Effluent pH	8.9	0.1
Neutraliser usage, kg/cu m	0.91	0.04
Neutraliser usage, lbs/1000 gal	7.9	0.3
Neutraliser usage, g/cu m/ppm influent acidity	0.68	0.1
Cost, cents/1000 gal	13.2	0.5
Cost, cents/cu m	3.49	0.1
Cost, cents/10^3cu m/ppm influent acidity	7.71	1.1
Utilisation efficiency, percent	54	5
Stoichiometric factor (influent acidity)	2.70	0.4
Sludge to waste, % of influent AMD	2.1	1.1
Sludge recycled, % of influent AMD	0	0
Dry solids recycled, lbs/1000 gal	0	0
Dry solids to waste, lbs/1000 gal	7.4	0.6
Dry solids to waste, kg/cu m	0.89	0.1
Underflow solids, percent	9.1	0.1
Effluent turbidity, JTU	26	4
Reactor suspended solids, mg/l	1300	200
Effluent suspended solids, mg/l	23	9

Table 11. NEUTRALISATION DATA SUMMARIES FOR Line @ 1 LITER/SEC (16 GPM) WITH NO AERATION USING COAGULANT ADDITION

	Mean	Std. Dev.
Effluent pH	8.9	0.1
Neutraliser usage, kg/cu m	0.91	0.1
Neutraliser usage, lbs/1000 gal	7.56	0.J
Neutraliser usage, g/cu m/ppm influent acidity	1.79	0.2
Cost, cents/1000 gal	13.2	0.4
Cost, cents/cu m	3.50	0.1
Cost, cents/10^3cu m/ppm influent acidity	6.90	0.9
Utilisation efficiency, percent	46	6.2
Stoichiometric factor (influent acidity)	2.17	0.7
Sludge to waste, % of influent AMD	2.23	0.1
Sludge recycled, % of influent AMD	19.9	0.7
Dry solids recycled, lbs/1000 gal	59	22
Dry solids to waste, lbs/1000 gal	6.6	2.4
Dry solids to waste, kg/cu m	0.79	0.3
Underflow solids, percent	3.97	1.2
Effluent turbidity, JTU	17	4.8
Reactor suspended solids, mg/l	9500	3500
Effluent suspended solids, mg/l	37	12

Table 14. NEUTRALIZATION DATA SUMMARIES FOR LIME @ 0.95 LITER/SEC (15 GPM) WHERE PROCESS B UTILIZED OXIDATION; PROCESS A HAD NO OXIDATION; BOTH USED COAGULANTS

	Process	Mean	Std. Dev.
Effluent pH	A	8.00	0.1
	B	8.05	0.1
Neutralizer usage, kg/cu m	A	.039	0.1
	B	.036	0.1
Neutralizer usage, lbs/1000 gal	A	7.84	0.5
	B	7.61	0.8
Neutralizer usage, g/cu m/ppm influent acidity	A	2.05	0.3
	B	2.01	0.2
Cost, cents/1000 gal	A	13.71	0.7
	B	13.07	1.5
Cost, cents/cu m	A	3.62	0.2
	B	3.45	0.4
Cost, cents/10^3cu m/ppm influent acidity	A	7.21	1.2
	B	7.05	0.0
Utilization efficiency, percent	A	40	5.4
	B	39	5.1
Stoichiometric factor (influent acidity)	A	0.77	0.4
	B	0.74	0.3
Sludge to waste, % of influent AMD	A	0.33	0.3
	B	0.35	0.1
Sludge recycled, % of influent AMD	A	20.0	1.1
	B	20.3	0.8
Dry solids recycled, lbs/1000 gal	A	36	10
	B	65	17
Dry solids to waste, lbs/1000 gal	A	7.1	3.3
	B	6.9	2.2
Dry solids to waste, kg/cu m	A	0.85	0.4
	B	0.83	0.3
Underflow solids, percent	A	1.6	1.3
	B	1.6	1.3
Effluent turbidity, JTU	A	80	3.8
	B	5	0.7
Influent suspended solids, mg/l	A	9250	3200
	B	7950	8600
Effluent suspended solids, mg/l	A	80	11
	B	6.0	5.5
Difference in reagent usage between Process A and B, percent		0.3	

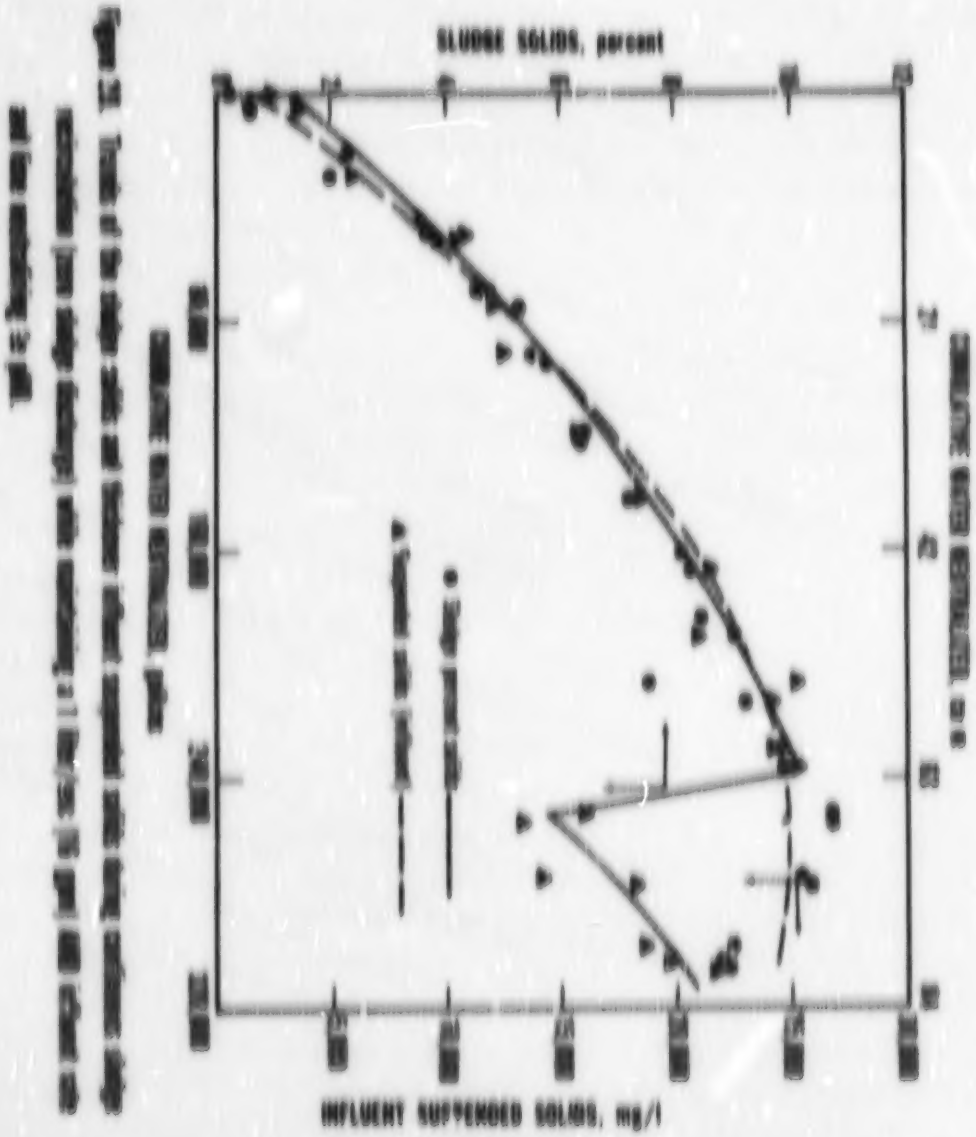
at 0.33 liter/sec (5.5 gpm), which corresponds to a 5%-percent (of the influent AMD) recycling rate. No sludge was discharged to waste. The influent suspended solids and sludge percent solids were monitored in order to observe the effects of the increasing solids concentration on the sludge density. As shown in Figure 20, both the influent suspended solids and the sludge percent solids increased uniformly until the sludge solids briefly leveled off and then radically dropped. The influent suspended solids lowered after the sludge solids dropped because less solids per unit volume were being recycled. After dropping to approximately 5 percent, the sludge percent solids began to increase again at approximately the same rate as was observed in the early part of the test. Unfortunately, the test was quite time-consuming and could not be continued.

It is felt that the drop in the sludge solids was caused by rat-holing in the sludge hopper of the thickener. It is conjectured that the sludge reached a density and viscosity sufficient to impede effective movement into the pump intake and as a result, the pump withdrew a column of water extending from the intake to the top of the sludge bed and found the less dense sludge easier to draw than the sludge immediately surrounding the intake.

Approximately 1900 liters (500 gal) of sludge resulted from the neutralization of approximately 1100 cu m (300,000 gal) of AMD. On a mass balance basis, approximately 725 kg (1600 lb) of dry solids should have resulted from the neutralization; approximately 360 kg (800 lbs) remained in the thickener hopper when the supernatant water was decanted.

IRON OXIDATION

AMD containing ferrous iron levels greater than 50 mg/l usually requires aeration during the neutralization process to oxidize the iron to the ferric form for precipitation. To design an aeration system, it is necessary to have a good estimate of the ferrous iron oxidation rate. The complexity of the iron oxidation process is well known.[10-15] Almost all the process parameters (e.g., pH, dissolved oxygen level, air bubble size, amount of light, types and concentrations of micro-organisms, temperature, as well as the concentrations of such ions as ferrous iron, ferric iron, aluminum, manganese, copper, aluminum, and silica) affect the oxidation rate in one manner or another. Of these parameters, pH, ferrous iron content, and dissolved oxygen concentration have the greatest influence. Only pH can be


SLUDGE SOLIDS, percent
INFLUENT SUSPENDED SOLIDS, mg/l

controlled, since the aerator should saturate the water with oxygen and the influent ferrous iron level is predetermined.

Only limited data on rate constants for AMD oxidation by aeration at neutral or basic pH's have been presented in the literature. Most of these rate constants were developed from either synthetic AMD or non-AMD solutions evaluated in laboratory studies. Unfortunately, valid extrapolation of laboratory data from synthetic solutions to real-world situations is often a difficult task.

Initial designs for the Crown facility were based on field oxidation studies at the test site using the AMD to be treated. The results of the field study were then compared with values from the literature and wide discrepancies were noted. These discrepancies prompted the design of a flexible oxidation system including considerable over-capacity to cover most contingencies. Even so, the detention capacity was insufficient for several of the tests made during the course of these investigations.

Typical ferrous decline curves were generated from laboratory oxidation tests (Figure 21) and illustrate the relative effects of treatment pH on the oxidation.

In 1974, EPA conducted a limited investigation on the oxidation process and included field observations on nine treatment plants.[10] The major conclusions from these investigations were as follows:

> --Few, if any, of the aeration systems achieved complete oxidation of the ferrous iron prior to entering the sedimentation basin. Complete oxidation in the aeration tank would seem desirable but in reality was not necessary in the cases observed because the water went to sizable lagoons where the oxidation was eventually completed. Where thickeners are used, complete oxidation in the aerator (to 1 mg/l or so) is a necessity because detention times in the thickeners are short.
>
> --Time-cyclic feeding of the neutralising reagent was common but was detrimental to aerator performance unless the frequency was closely spaced. Aeration systems performing unsatisfactorily could be improved by constant neutraliser addition.
>
> --All the facilities visited suffered from poor mixing in the oxidation systems as evidenced by massive accumulations of

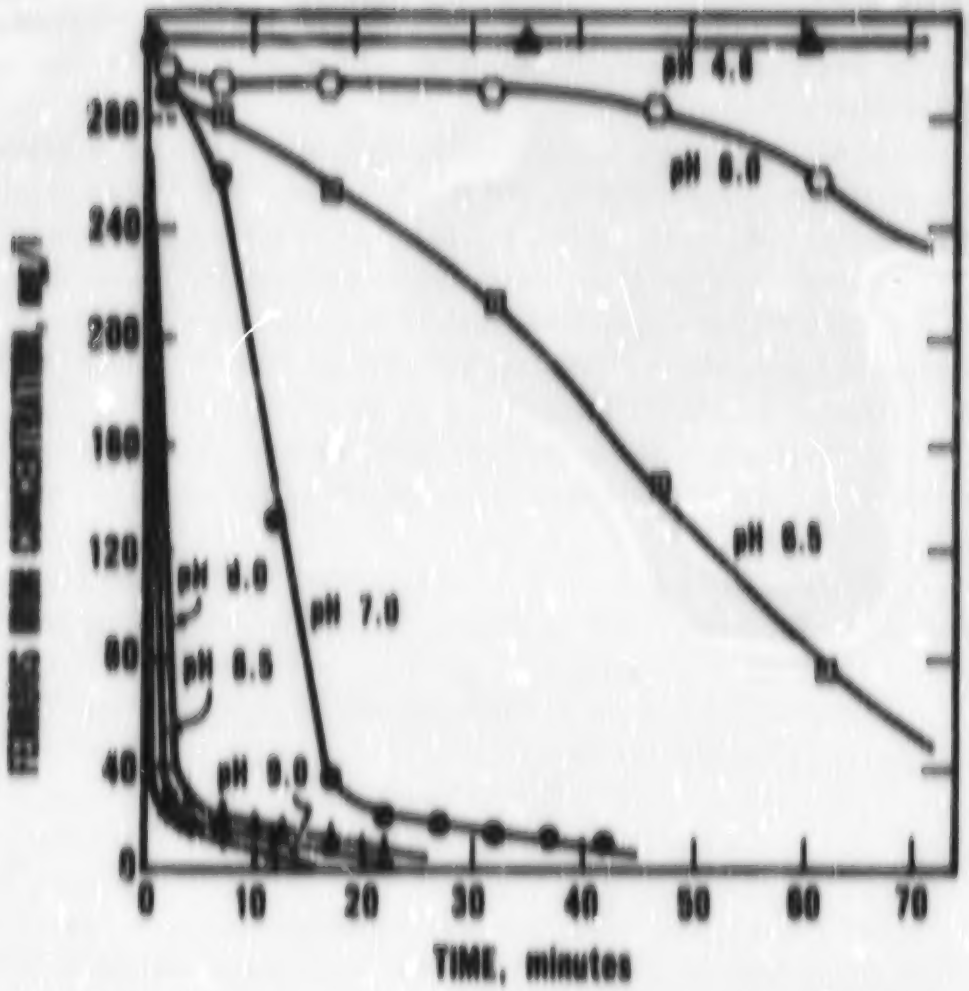


Figure 21. Ferrous decline of various pH's for the EPA Crown discharge as determined in the laboratory.

solids in the bottoms and around the periphery of the aeration tanks or ponds. These accumulations grossly reduced the detention times and contributed to short-circuiting and inefficient oxygen transfer. Use of intermittent lime addition further complicated the inadequacy of the processes. Oxidation ponds over half-full of solids were common. Increased mixing capability in terms of either bottom turbines and/or peripheral mixers must be incorporated into existing and future plants in order to eliminate this condition.

--A review was made of the current literature relative to oxidation rates in AMD treatment situations. No satisfactory guidelines were available to reliably predict the required oxidation time for an aeration system. EPA empirically developed a generalised equation for the oxidation time requirement as a function of treatment pH and ferrous iron content:

$$t = \frac{1}{k} \ln \frac{C_o}{C}$$ where C_o = initial ferrous conc. in mg/l
C = final ferrous conc. in mg/l
t = time, in minutes
$k = 3.17883 \times 10^{-7}(pH)^{6.4075 \pm 1.6492}$/min

This equation was developed from laboratory batch studies using nine different AMD waters. Even though the batch-type test data from each site conformed to first-order rate reaction procedures, the resulting rate constants differed significantly for each site visited. Also, the batch-test data did not correlate well with observed conditions at operating treatment plants in the field. Considering all inequities, however, the equation could be useful for preliminary estimates and trouble-shooting in relation to oxidation problems. It must be emphasised that individual on-site tests should be made on the AMD to be treated before designing an aeration system and that some difficulty may be encountered in accurately extrapolating these data to full-scale conditions.

Oxidation data from the current pilot-plant studies involving lime and limestone treatment under the wide range of conditions investigated at Orum were tested for conformance to first-order rate reaction characteristics. Too much variance was present to reliably apply first-order reaction procedures. These data were then grouped together and the average oxidation rates were calculated for each of 140 different data sets. Figure 22 shows the compilation of the data where the average rate is expressed as a function of treatment pH. Linear regression analyses of the data generated the equation:

Average oxidation rate, mg/l per min = 2.03(pH)-8.26

Again, considerable scatter is evident in the data in Figure 22. Assuming normal neutralization techniques would treat to a minimum of pH 7, a rough estimate of the average oxidation rate for design purposes on influent ferrous irons below 300 mg/l would be 6 mg/l per minute. Use of this figure should provide considerable overcapacity in the majority of situations; however, overcapacity in the pollution abatement field should be the rule rather than the exception in order that most contingencies can be accommodated. As was observed in the earlier EPA oxidation report,[10] the nine sites visited probably had adequate oxidation capability when the plants started; but increases in flow because of constantly expanding mine area, decreases in water quality because of increases in pyritic contact, and deterioration of the effectiveness of the aeration system because of solids accumulation all led to a general decline in the overall effectiveness of the process. It is felt that it would be cheaper to overdesign in the first place than to retrofit expanded facilities in an existing plant.

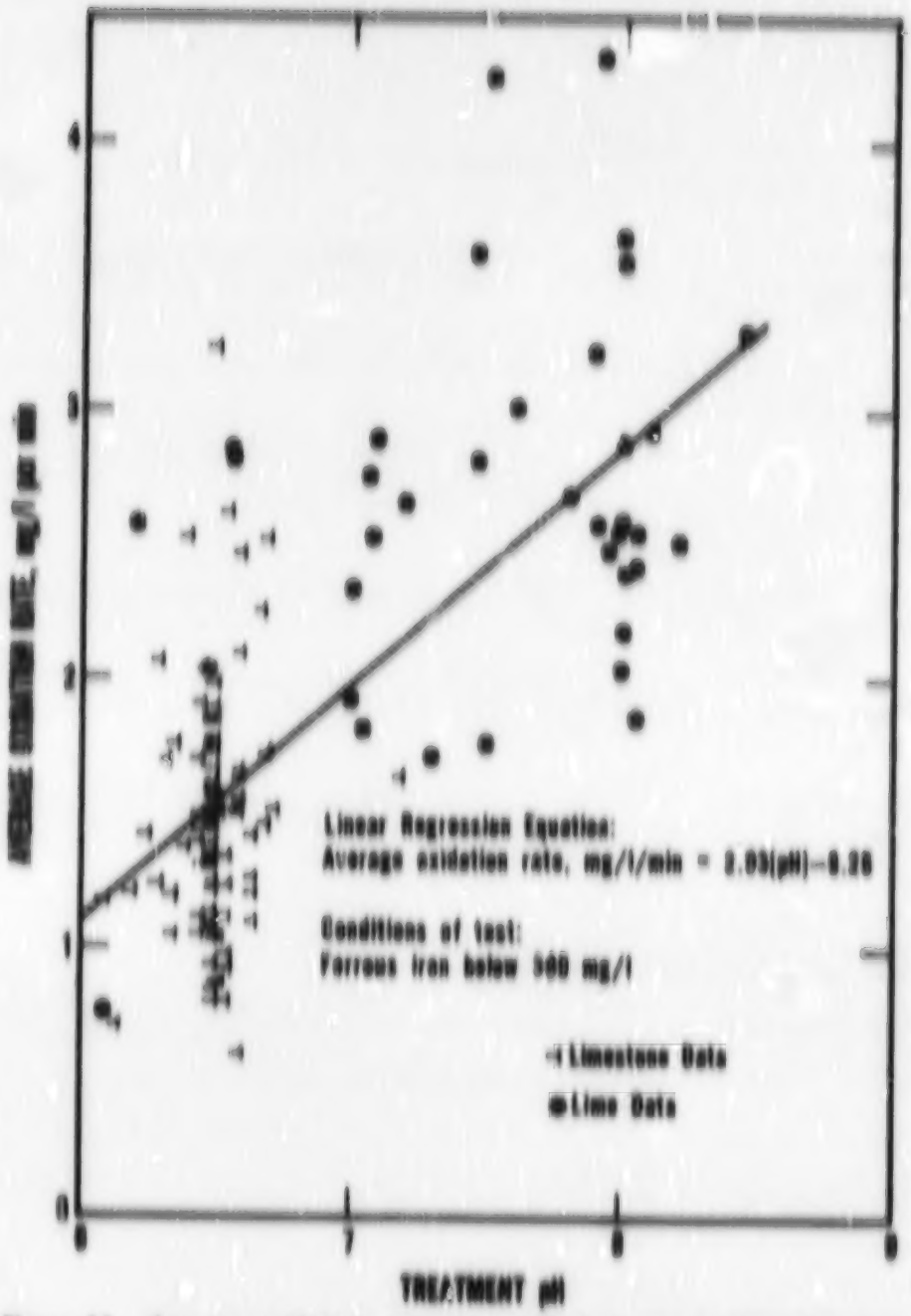


Figure 22. Average oxidation rates from 140 data sets of limestone and of lime neutralization shown as a function of the treatment pH.

REFERENCES

1. Wilmoth, Roger C., Lime and Limestone-Lime Neutralization of Acid Mine Drainage, U.S. Environmental Protection Agency Report 670/2-74-091, Cincinnati, Ohio. 1974.

2. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes. 1971.

3. Dunk, R., M. A. Mostyn, and H. C. Hoare, General Procedure for Indirect Determination of Sulfate, Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corporation, Norwalk, Connecticut. March 1971.

4. U.S. Steel Corporation, Sampling and Analyses of Coal and Coke and By-products, Third Edition, 1929.

5. Galotto, R. V., et al., Procedure for Determination of Mine Waste Acidity, paper given at the 154th National Meeting of the American Chemical Society, Chicago, Illinois. 1966.

6. Bituminous Coal Research, Inc., Studies on Limestone Treatment of Acid Mine Drainage, Federal Water Quality Administration, Research Series 14010 EIS 01/70, Washington, D. C. 1970.

7. Singer, Philip C. and Werner Stumm, Kinetics of the Oxidation of Ferrous Iron, Second Symposium on Coal Mine Drainage Research, May 1968, Pittsburgh, Pennsylvania.

8. Ford, Charles, personal communication. June 1975.

9. Hill, Ronald D., personal communication. September 1975.

10. Wilmoth, Roger C., James L. Kennedy, and Ronald D. Hill, Observations on Iron Oxidation Rates in Acid Mine Drainage Treatment Plants, Fifth Symposium on Coal Mine Drainage Treatment Research, October 1975, Louisville, Kentucky.

11. Stumm, Werner, Oxygenation of Ferrous Iron, First Symposium on Acid Mine Drainage Research, Pittsburgh, Pennsylvania. May 1965.

12. Kim, Ann G., An Experimental Study of Ferrous Iron Oxidation in Acid Mine Water, Second Symposium on Coal Mine Drainage Research, Pittsburgh, Pennsylvania. May 1968.

13. Mihok, E. A., and C. E. Chamberlain, Factors in Neutralising Acid Mine Waters with Limestone, Second Symposium on Coal Mine Drainage Research, Pittsburgh, Pennsylvania. May 1966.

14. Holland, Charles T., James L. Corsaro, and Douglas J. Ladish, Factors in the Design of an Acid Drainage Treatment Plant, Second Symposium on Coal Mine Drainage Research, Pittsburgh, Pennsylvania. May 1966.

15. Holland, Charles T., Robert C. Berkshire, and Daniel F. Golden, An Experimental Investigation of the Treatment of Acid Mine Water Containing High Concentrations of Ferrous Iron with Limestone, Third Symposium on Coal Mine Drainage Resea' , Pittsburgh, Pennsylvania. May 1970.

16. Helmcost, Joseph G., The Design of Oxidation Systems for Mine Water Discharges, Fourth Symposium on Coal Mine Drainage Research, Pittsburgh, Pennsylvania. April 1972.

17. Lovell, Harold L., An Appraisal of Neutralization Processes to Treat Coal Mine Drainage, U.S. Environmental Protection Agency Technology Series Report, EPA-670/2-73-093, Washington, D. C. November 1973.

18. Singer, Philip C., and Werner Stumm, Oxygenation of Ferrous Iron: The Rate-Determining Step in the Formulation of Acidic Mine Drainage, U.S. Environmental Protection Agency Water Pollution Control Research Series Report, DAST-26, 14010 06/69, Washington, D. C. June 1969.

19. Mihok, Edward A., Plant Design and Cost Estimates for Limestone Treatment, U.S. Dept. of Interior Mine Water Research Series, U.S. Bureau of Mines RI 7366, Washington, D. C. April 1970.

GLOSSARY

CALCULATIONS AND DEFINITIONS

Mean Probable Detention Time: A mathematical approximation of the average actual time a flowing liquid is detained in a vessel. The value is determined by tracer studies in which the tracer concentration exiting from the tank is monitored in respect to time. Two values are plotted on probability paper for each measurement point; i.e., cumulative tracer quantities to each point divided by the total cumulative tracer quantity measured (percent passing) and the ratio of elapsed time of each measurement divided by the theoretical detention time of the vessel. The theoretical time equals the tank volume divided by the flow rate. The resulting probability plot is interpolated to derive the time for 50-percent passing.

Detention Efficiency: The ratio of mean probable detention time to theoretical detention time expressed as a percentage.

Utilisation Efficiency: A measure of the proportion of a neutraliser that reacts with the acid water as compared to the amount originally added. Since alkalinity imparted to the water is considered a benefit, the formula for utilisation efficiency is:

$$\text{Utilisation Efficiency} = \frac{\text{Alkalinity Used}}{\text{Alkalinity Added}}$$

therefore,

$$\text{Utilisation Efficiency} = \frac{\text{Influent Acidity} - \text{Effluent Acidity} + \text{Effluent Alkalinity (all as } CaCO_3)}{\text{Alkalinity Added (as } CaCO_3)} \times 100$$

Stoichiometric Factor: The ratio of amount of neutraliser required to treat the original amount of acid present:

$$\text{Stoichiometric Factor} = \frac{\text{Alkalinity Added (as } CaCO_3)}{\text{Influent Acidity (as } CaCO_3)}$$